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# ANALYTICAL ABSTRACTS

## 1.—GENERAL ANALYTICAL CHEMISTRY

*General reviews of progress, reagents and methods of general application.*

3367. **Seventh Colloquium Spectroscopicum Interonale. September, 1958.** Organised by the ociation des Ingénieurs sortis de l'Université de ge. *Rev. Univ. Min.*, 1959, **15** (5).—The follow- papers of analytical interest are published (in nch unless otherwise stated). **Infra-red spectroy and its applications to industry,** H. W. Thomp- 225–230. **The present state and future pros-s in emission spectroscopy,** W. F. Meggers, –237 (in English). **New methods in spectroscopic niques (possibilities of interference spectroscopy),** Jacquinot, 237–249. **Evolution of emission tral techniques in industrial control in Belgium,** Mathieu and A. Hans, 250–256. **Infra-red tra between 1·1 and 2·5 microns,** G. Hepner, –258. **Analysis of bands of a new system attrib-l to the molecule $N_2^+$,** J. Janin and J. d'Incan, –261. **Ratio of the intensity of the components he doublets in the spectra of aluminium, indium thallium,** D. 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Descamps, 539–543. **Rapid analysis of copper, zinc and cobalt by X-ray fluorescence in mineral powders and concentrates,** A. Hans, 544–548. **X-ray fluorescence analysis of powders,** F. J. Haftka, 549–555 (in German). **Quantitative analysis by X-ray fluorescence: detection of niobium in complex minerals,** M. Mariee, 555–558. **Nuclear and electronic magnetic resonance,** B. Bleaney, 559–563 (in English). **Spectral determination of carbon and sulphur in industrial control,** V. Mathieu and M. Lacomble, 597–598.

3368. **X-ray fluorescence spectroscopy in chemical analysis.** E. T. Hall. *Endeavour*, 1959, **28**, 83–87.—A review.

3369. **A mixture of aqua regia and potassium iodide as oxidation agent and solvent.** D. Prístavka (Dept. Anal. Chem., High-School of Chem. Technol., Bratislava, Czechoslovakia). *Chem. Zvesti*, 1958, **12** (11), 682–683.—A mixture of KI, $HNO_3$ and

HCl has been found useful for dissolving various materials, *e.g.*, alloys, special steels, pyrites. *Procedure*—Mix the sample with an equal amount of KI and add aqua regia dropwise (violent reaction); then add 2 to 3 ml of aqua regia in excess and heat. Dissolution is complete within 20 min. Sodium iodide must be used in place of KI when dissolving platinum alloys, to prevent the formation of slightly sol. potassium salts. When dissolving pyrites or sulphur-containing organic compounds, the sample is treated with KI and 5 to 6 ml of $HNO_3$ and, after 2 min., 3 ml of conc. HCl is added. No separation of elementary sulphur has been observed.

J. ZÝKA

3370. **The analytical use of diarylboric acids [diarylborinic acids] and especially of tetraphenyl diboroxide.** R. Neu (Arzneimittelfabrik Dr. W. Schwabe, G.m.b.H., Karlsruhe-Durlach, Germany). *Chemist Analyst*, 1958, **47** (4), 106–109.—The properties of the diarylborinic acids are discussed, and directions are given for the preparation of tetraphenyl diboroxide and 2-aminoethyl- and 2-amino-2-methyl-1-propyl-diphenylborate, and for their use in the detection of hydroxyphenylbenzo-δ-pyrones, of choline and -onium compounds, and of surface-active compounds, and for the determination of 8-hydroxyquinoline and of flavones.

R. E. ESSERY

3371. **Steric hindrance in analytical chemistry. V. A new 2-substituted 8-hydroxyquinoline (oxine).** H. Irving and D. J. Clifton (Inorg. Chem. Lab., Oxford Univ.). *J. Chem. Soc.*, 1959, 288–290.—2-(1-Ethylpropyl)-8-hydroxyquinoline (**I**) is prepared (method described) and the sensitivity of its reaction towards $Cu^{2+}$, $Zn^{2+}$, $Al^{3+}$ and $In^{3+}$ is compared with that of 2-methyl- (**II**), 2-phenyl- (**III**), 5-methyl- and unsubstituted 8-hydroxyquinoline. The sensitivity is determined in buffers at pH 5·14, 8·4 and 12·4. The sensitivity of **I** for $Cu^{2+}$ and $Zn^{2+}$ is comparable with that of **II** and **III**, and like all 2-substituted oxines it gives no ppt. with $Al^{3+}$. With $In^{3+}$, **I** gives a ppt. even at pH 12·4 and this is accounted for by the "weighting effect" and the higher basicity which more than compensates for the steric effect.

E. J. H. BIRCH

3372. **4-(2-Pyridylazo)resorcinol as a possible analytical reagent for the colorimetric determination of cobalt, lead and uranium.** F. H. Pollard, P. Hanson and W. J. Geary (Dept. of Phys. and Inorg. Chem., Univ. of Bristol, England). *Anal. Chim. Acta*, 1959, **20** (1), 26–31.—This reagent (preparation described) gives colours with many heavy-metal ions, but not with ions of the alkaline-earth and alkali metals. It is claimed to be valuable for the colorimetric determination of Co, Pb and U, since it has high sensitivity and is soluble in water.

W. T. CARTER

3373. **Application of thio salts in analysis. IV. A new scheme of qualitative analysis. Part C.** G. B. S. Salaria (Chem. Dept., Gov. Coll., Rohtak, Punjab, India). *Anal. Chim. Acta*, 1958, **19** (6), 605–606.—Observations on an earlier scheme (*Anal. Abstr.*, 1956, **3**, 1599) include suggestions for improving efficiency and new procedures for the detection of metals of the copper group and the iron - aluminium group in the presence of phosphate.

T. R. ANDREW

3374. **Thermal stability of analytical standard VI.** C. Duval (Lab. de Recherches Micro-Ana École Nat. Supérieure de Chim., Paris). *Ana Chim. Acta*, 1959, **20** (1), 20–25 (in French).—Th thermolysis curves and i.r. absorption spectra of th following substances have been determined- $NaNO_2$, $SrS_2O_3.H_2O$, $Na_3H_2IO_6$, $AlCl_3.6H_2O$, $K_2S_2O$ $Na_2S_2O_7$, $FeSO_4.7H_2O$, nitrilotriacetic acid, molyl dophosphoric acid, aluminium ammonium sulphat ammonium ferrous sulphate and ammonium ferr sulphate.

W. T. CARTER

3375. **New pH indicator.** M. Z. Barakat, S. E Shehab and M. M. El-Sadr (Biochem. Dept., Fa of Vet. Med., Giza, Cairo). *Analyst*, 1958, **8** 695–696.—A new pH indicator is prepared b condensing Na 1:2-naphthaquinone-4-sulphonat with 2:4-dinitrophenylhydrazine. The colou change is from rose-red at pH values below 8· to violet at values above 9·2. The indicator ha been used in determining the acidity of urine an vinegar, the acid value of oils and water-inso organic acids and also in the urease test. It is no suitable for titrating free $H_2SO_4$ in a soln. of CuSO or for assaying vegetable alkaloids. It form crimson crystals with strychnine, a purple - viole colour with brucine and an intense blue colour wit atropine. It can be used for the differentiation o strychnine and brucine.

A. O. JONES

3376. **Omega Chrome black PPV [C.I. Mordan Black 39], a new metal indicator.** A. A. Abd E Raheem and Abdel-Aziz Amin (Min. of Publi Health Lab., Cairo, Egypt). *Z. anal. Chem* 1959, **165** (6), 416–421 (in English).—The use o Omega Chrome black PPV is described for th EDTA titration of Zn, Mn, Ni, Cd, Mg and Pb The limits of detection of the end-points wer determined and the accuracy of titration wa ±1%. The indicator was suitable for the titratio of mixtures of Mn and Zn, the error being >1% The colour reactions of 20 metals with the indicato are listed.

G. P. COOK

3377. **Preparation of stable standard sulphato cerate solutions.** S. Carrano and A. F. McGuin (Dept. of Chem., Fairfield Univ., Conn., U.S.A.) *Chemist Analyst*, 1958, **47** (4), 103–104.—For th preparation of stable sulphatocerate soln., the hea of dilution of the $H_2SO_4$ should be fully utilised and dilution carried out slowly. To 200 ml o conc. $H_2SO_4$ add 700 g of ceric ammoniu sulphate, mix to a slurry and allow to stand fo 24 hr., with occasional stirring. Then mak successive additions of 250-ml portions of wate with manual stirring, allowing the temperature t develop fully between each addition, as shown by thermometer. When the vol. has reached 3 litres complete the dissolution, if necessary, by heatin at 60° till the soln. is perfectly clear. Cool to roo temp., and add water slowly, with vigorous swirling till the vol. reaches 10 litres. Soln. so prepare (0·1 *N* in 1·0 *N* $H_2SO_4$) have remained clear, stable and constant in titre for at least 12 months.

R. E. ESSERY

3378. **Manganimetry. I. Preparation, standardisation and stability of manganic pyrophosphat solution.** Masayoshi Ishibashi, Tsunenobu Shig matsu and Shozo Shibata (Chem. Dept., Kyot Univ., Sakyo-ku, Tokyo). *Japan Analyst*, 195 **7** (10), 644–646.—Standard $MnHP_2O_7$ soln. is prepare by treating $MnCl_2$ (12·5 g) in 3 *M* $K_4P_2O_7$ (100 m with $KMnO_4$ (1 g). The $MnO_2$ is filtered off, th

rate brought to pH 4·5 with *N* NaOH, the $MnO_2$ is filtered off, and the filtrate is made acid th $H_2SO_4$ (1:1) to remove $K_2SO_4$, and stored at I 4 to 6. The oxidation of $Mn^{2+}$ is also effected th conc. $HNO_3$ (10 ml) by heating to dryness and ishing the residue with acetone and ether. The oduct dissolved in water gives the same absorption rve as that prepared by Belcher and West's ethod (*Anal. Chim. Acta*, 1950, **6**, 322). For the andardisation, $(NH_4)_2SO_4.FeSO_4.6H_2O$ is the best agent.

**II. Direct oxidimetric titration of quinol with anganic pyrophosphate.** Masayoshi Ishibashi, unenobu Shigematsu and Shozo Shibata. *Ibid.*, 58, **7** (10), 647–649.—Quinol (3 to 10 mg) is rated with $MnHP_2O_7$ soln. (0·03 to 0·07 *N*) in 2 to N $H_2SO_4$, either potentiometrically at −0·5 V the S.C.E. or with diphenylamine soln. (0·2%, 2 ml) as indicator. In >7 *N* $H_2SO_4$ or >5 *N* Cl, *p*-benzoquinone interferes. K. Saito

3379. **The EDTA titration: applications. V. nclusion.** H. Flaschka, A. J. Barnard, jun., and . C. Broad (Dept. of Chem., Georgia Inst. of echnol., Atlanta, U.S.A.). *Chemist Analyst*, 1958, (4), 109–112.—A literature survey is presented, hich covers the determination of pharmaceutical d organic compounds, the analysis of biological aterials, the determination of the hardness of ater, recent developments in the use of dyes and her organic compounds as indicators for the EDTA ration, and the radiometric detection of the end-oint. (97 references.) R. E. Essery

3380. **EDTA titrations without metal indicators.** uddhadev Sen (Coates Chem. Lab., Louisiana tate Univ., Baton Rouge, U.S.A.). *Anal. Chim. cta*, 1958, **19** (6), 551–554.—Metal ions whose DTA complexes have formation constants >15 ay be titrated by adding an excess of EDTA isodium salt) and back-titrating with standard $^{2+}$ soln. The test soln. (≃25 ml) should be at H 7; 1 ml of saturated $NH_4SCN$ soln. and an equal ol. of acetone are added. The appearance of the ue cobalt thiocyanate colour marks the end-point. ood results are reported for $Th^{4+}$, $Pb^{2+}$, $Ni^{2+}$ and $O^{2+}$; $Hg^{2+}$ and $Cu^{2+}$ cannot be titrated by this ethod. T. R. Andrew

3381. **Complexometric titrations (chelatometry). L. Back-titration, with pyrogallol red or bromo-yrogallol red as indicator.** M. Malát, V. Suk and . Tenorová (Inst. Anal. Chem., Charles' Univ., rague). *Chem. Listy*, 1958, **52** (12), 2405–2407.—*ack-titration with* $Bi(NO_3)_3$—Dilute the soln. of $d^{2+}$, $Tl^{3+}$, $Fe^{3+}$, $In^{3+}$, $Ga^{3+}$ or $Bi^{3+}$ (in the form of trates) to 100 ml and add an excess of EDTA isodium salt) (**I**) (0·05 to 0·01 *M*). Adjust the H to 2 to 3, add pyrogallol red soln. (**II**) or bromo-yrogallol red soln. (**III**) (0·05% in 50% ethanol) 5 drops) as indicator and titrate the yellow soln. ith 0·1 *M* $Bi(NO_3)_3$ till red or violet - red; add the 1 *M* $Bi(NO_3)_3$ in slight excess and titrate back th **I** till yellow, to increase the accuracy in the termination of the end-point; 1 to 10 mg of Pd, to 35 mg of Tl, 0·6 to 100 mg of Fe, 0·1 to 170 mg In, 0·3 to 85 mg of Ga and 2 to 100 mg of Bi n be determined; Zn, Mn, Cd, Ag, Be, Ge, rare-d alkaline-earth metals and $NH_4^+$ do not inter-re. In the presence of Ni, Al, Cu and Hg, the ration must be carried out at a higher temp. An cess of $Hg^{2+}$ can be removed by the addition of corbic acid. Coloured ions (Co, Cu, Ni, Cr and interfere when present in excess; Pd can be determined in the presence of Pt, Rh and Ir. *Back-titration with* $Pb(NO_3)_2$—Dilute the sample of $Pd^{2+}$, $Ni^{2+}$, $Ga^{3+}$, $In^{3+}$, $Bi^{3+}$, $Tl^{3+}$, $Fe^{3+}$, $V^{4+}$, $Cu^{2+}$, $Th^{4+}$, $Co^{2+}$ or $Pb^{2+}$ to 100 ml, add an excess of **I**, together with indicator, adjust the pH to 5, add Na acetate soln. (20%) (5 to 6 ml) and titrate with 0·05 to 0·01 *M* $Pb(NO_3)_2$ till violet (**II**) or blue - violet (**III**); add a slight excess of the $Pb(NO_3)_2$ soln. and titrate with **I** till red; 0·5 to 10 mg of V, 1 to 10 mg of Pd, 1·5 to 35 mg of Tl, 0·5 to 30 mg of Fe, 0·6 to 16 mg of Cu, 1 to 23 mg of In, 3 to 13 mg of Ga, 2 to 180 mg of Th, 0·6 to 30 mg of Ni, 0·5 to 30 mg of Co, 2 to 100 mg of Bi and 2 to 200 mg of Pb can be determined. The presence of Ca, Ba, Mg and Sr causes no interference if **II** is used as indicator; Li, K, Ag, Cr, $NH_4^+$, $Cl^-$, $ClO_4^-$, $NO_3^-$ and $SO_4^{2-}$ do not interfere even when present in 500 to 1000-fold excess. The average error in both procedures is ±0·2%. The method has been applied to the analysis of an alloy of Ag and In (9:1). J. Zýka

3382. **Tetraethylenepentamine, a selective titrant for metal ions. Potentiometric end-point detection.** C. N. Reilley and A. Vavoulis (Dept. of Chem., Univ. of N. Carolina, Chapel Hill, U.S.A.). *Anal. Chem.*, 1959, **31** (2), 243–248.—Methods are given for the titration of Hg, Cu, Ni, Zn and Cd, singly and in various mixtures, with tetraethylenepentamine (**I**) and a mercury electrode for potentiometric end-point detection. The alkaline-earth and rare-earth metals, Al, Bi, Pb and Sc do not interfere. The reaction of **I** with the elements quoted is discussed theoretically in relation to the effect of pH, complex formation and hydrolysis. It is shown that potential *vs.* pH diagrams obtained when a mercury electrode is used give a means of predicting optimum titration conditions and of detecting the relative effect of competing equilibria. On theoretical and practical grounds it is shown that **I** is superior to triethylenetetramine as a selective titrant for metal ions. F. L. Selfe

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*See also Abstract*—**3523**, Removal of $H_2SO_4$ from $H_3PO_4$.

## 2.—INORGANIC ANALYSIS

*General, determination of elements (arranged in the order of the Periodic Table), analysis of minerals and inorganic industrial products.*

3383. **Direct titration of hydrochloric - sulphuric acid and nitric - sulphuric acid mixtures in acetone. Automatic derivative potentiometric or spectrophotometric end-point detection.** H. V. Malmstadt and D. A. Vassallo (Univ., Urbana, Ill., U.S.A.). *Anal. Chem.*, 1959, **31** (2), 206–210.—In the procedures given, the proton from HCl or $HNO_3$ and the first proton from $H_2SO_4$ are titrated together to the first end-point. The second proton from $H_2SO_4$ is then titrated to the final end-point. The titration is made with tri-*n*-butylmethylammonium hydroxide (0·1 *N* soln. in dry benzene) on a 5- or 10-ml aliquot of the sample soln. in the presence of acetone (90%). Both end-points are sharp and can be determined successively, to within 0·01 ml, either potentiometrically with platinum (10% Rh) - graphite electrodes or spectrophotometrically at 575 mμ, using in each instance the automatic derivative method. For high accuracy a correction should be made for the amount of acetic acid in the

acetone and of $CO_3^{2-}$ in the titrant. For concn. of $H_2SO_4$, HCl and $HNO_3$ of $\simeq 0{\cdot}5$ milli-equiv. each, the error is $\simeq \pm 0{\cdot}3\%$ for each acid.

W. J. Baker

3384. **Ion-exchange separation of metal ions.** J. S. Fritz and G. R. Umbreit (Inst. for Atomic Res., Iowa State Coll., Ames, U.S.A.). *Anal. Chim. Acta*, 1958, **19** (6), 509–516.—Separation of metal ions can be effected by cation-exchange resins in the presence of EDTA at a pH such that one ion is firmly complexed and another almost completely dissociated. Retention on a Dowex 50-X4 resin column is recorded against pH for $Bi^{3+}$, $Fe^{3+}$, $Zr^{4+}$, $Cu^{2+}$, $Sc^{3+}$, $Th^{4+}$, $Yb^{3+}$, $Hg^{2+}$, $Zn^{2+}$, $Y^{3+}$, $Sm^{3+}$ and $La^{3+}$. The effect of changing the column length and ion concn. is reported. Conditions are given for the separation of equimolecular mixtures of La and Th, Sm and Fe, Y and Sc, and Mg and Al.

T. R. Andrew

3385. **Ion-exchange separation of metals by a single-pass method.** R. T. Oliver and J. S. Fritz (Ames Lab., Ames, Iowa). *U.S. Atomic Energy Comm.*, Rep. ISC-1056, 1958, 4 pp.—A single-pass method for the ion-exchange separations of binary mixtures of metals is described, and experimental applications are presented. The method consists in complexing each of the components in the mixture with a separate complexing agent at a pH sufficient to ensure max. co-ordination of the metals. The complexing agents are chosen so that the metal complexes formed are of opposite charge. The mixture is then passed through an ion-exchange resin which adsorbs one species completely, allowing the other to be collected in the eluate. An anion- or cation-exchange resin is used. Sulphosalicylic acid was used to form a negative complex with Fe, U, Al, Th, Zr or Y. Ethylenediamine was used to form a positive complex with Cu, Zn, Ni or Cd. Quant. separations of binary mixtures containing one metal from each of these groups were performed at pH values 8, 9 and 10 with Dowex (nuclear sulphonic cation-exchange resin) and Amberlite IRA-401 (quaternary amine anion-exchange resin).

Nucl. Sci. Abstr.

3386. **Determination of copper, lead, tin and antimony by controlled-potential electrolysis. III. Adaptation of the method to the analysis of some alloys.** B. Alfonsi (Res. and Control Lab. Auto-Avio, FIAT, Turin, Italy). *Anal. Chim. Acta*, 1958, **19** (6), 569–575.—Previous work (*cf. Anal. Abstr.*, 1959, **6**, 2468) has been extended to cover the analysis of tin-base bearing alloys, leaded bronze, Ag - Cu - Cd - Zn alloys and Cu - Cd alloys.

T. R. Andrew

3387. **Potentiometric titration of silver, copper, lead and thallium with thioacetamide.** L. M. Andreasov, E. I. Vaĭl, V. A. Kremer and V. A. Shelikhovskiĭ (A. M. Gorky Kharkov State Univ.). *Zhur. Anal. Khim.*, 1958, **13** (6), 657–660.—The pptn. of metals by thioacetamide can be speeded up by an addition of a small amount of hydrazine hydrate, and this enables Cu, Pb and Tl to be determined potentiometrically. Such an addition is not necessary in the potentiometric determination of $Ag^+$ as sulphide, the pptn. being rapid enough in ammoniacal medium. For the determination of Cu, to a 10-ml aliquot of the sample soln. in dil. $HNO_3$ (containing 0·01 to 0·015 g of $Cu^{II}$) add 30 ml of *N* Na acetate and 5 ml of aq. $NH_3$ (25%), followed by hydrazine hydrate soln. (1 : 5), dropwise, until the blue colour is discharged. Then titra with thioacetamide. An excess of hydrazine hydra in the soln. should be avoided. Similar determin tions are described for Ag, Pb, Tl and mixtures Ag and Cu.

W. Roubo

3388. **Indirect mercurimetric determination cadmium, cobalt, nickel and zinc by means of the pyridine - thiocyanate complexes.** J. Bognár an S. Sárosi (II Chem. Dept., Tech. Univ. for Heav Ind., Miskolc, Hungary). *Magyar Kém. Foly* 1959, **65** (1), 28–30.—Details are given of a metho in which the metals are pptd. as complexes wit pyridine and $NH_4SCN$, with a composition varyin from $M(Py)_2(SCN)_2$ to $M(Py)_4(SCN)_2$. The ppt. dissolved in *N* $H_2SO_4$ and the $SCN^-$ are titrate with 0·1 *N* $Hg(NO_3)_2$ in the presence of $K_3Fe(CN$ and Xylenol blue VS (*cf.* Bognár and Jellinek, *Ana Abstr.*, 1958, **5**, 2623; Bognár, *Ibid.*, 1958, **5**, 3661 A determination takes 15 to 25 min.

A. G. Peto

3389. **Application of alginic acid as an ion ex changer. I. The separation and determination various metal ions [iron, aluminium and copper** Takeo Takahashi and Satoru Emura (Inst. Inc Sci., Tokyo Univ., Yayoicho, Chiba). *Japa Analyst*, 1958, **7** (9), 568–571.—The separation Fe$^{III}$, Al and Cu with alginic acid as ion exchange (Specker and Hartkamp, *Z. anal. Chem.*, 1953, **140** 167; Specker *et al.*, *Ibid.*, 1954, **141**, 33) was exam ined by the batch method. The time taken fo reaching the equilibrium state is $\simeq 5$ hr. for Fe an $\simeq 8$ hr. for Al. Dil. $H_2SO_4$ is used as eluting agen and $Fe^{3+}$, $Cu^{2+}$ and $Al^{3+}$, eluted in this order, ar determined complexometrically. The $K_d$ value fo Fe is almost independent of the amount of Al bu it decreases when the concn. of Fe is $>0{\cdot}001$ *M* Specker's results for the separation were confirmed

K. Saito

3390. **Rapid determination of iron, aluminium calcium and magnesium in the presence of manganes by the use of CyDTA [1:2-diamino*cyclo*hexanetetra acetic acid] and EDTA. Application to the analysi of basic open-hearth furnace slag.** Yoshihide End (Fukiai Plant, Kawasaki Steel Corp., Wakihama Fukiai-ku, Kobe). *Japan Analyst*, 1958, **7** (10) 611–616.—The EDTA titration of $Fe^{3+}$ at pH 1· to 2·2 with salicylic acid (**I**) as indicator and of A at pH 2 to 2·2 with Cu - 1-(2-pyridylazo)-2-naphtho (**II**) (*cf.* Flaschka and Abdine, *Anal. Abstr.*, 1957 **4**, 361) can be applied in the presence of Mn, C and Mg by using 1:2-diamino*cyclo*hexanetetra acetic acid (**III**). Provided that $Mn^{2+}$ are maske with EDTA, **III** does not interfere with the pptn of Ca oxalate at pH 3·5 to 4·2. The sum of Ca an Mg is titrated with EDTA in the presence of tri ethanolamine and KCN. The time taken for determination is $\simeq 50$ min. *Procedure*—Dissolve th sample in HCl (15 ml) and $H_2O_2$ (30%, a few drops) dilute to 150 ml and add ammonium acetate soln (25%, 10 ml) and HCl (1:1) or aq. $NH_3$ soln (1:1) to give a pH of 1·5. Heat the soln. to 30° add **I** (0·1 g) and titrate with 0·05 *M* **III** (for Fe) Add $Cu(NO_3)_2$ soln. (0·05 *M*, 1 ml), adjust the pH t 2 to 2·2 with ammonium acetate soln. (5%), boil, ad **II** soln. (0·1%, 2 to 3 drops) and titrate the ho soln. with 0·05 *M* **III** (for Al). Dilute the soln. t 250 ml, add EDTA (0·1 *M*, 5 to 10 ml) to a 100-m portion and aq. $NH_3$ soln. to make the pH 3·5 t 4·4 and boil with ammonium oxalate soln. (5% 20 ml) to precipitate Ca. Make another 100-m portion ammoniacal (pH 10) with $NH_4Cl$ soln

, 20 ml), triethanolamine (5 ml) and KCN 15 ml) and titrate with 0·05 *M* EDTA, with hrome black T as indicator (for the sum of Ca Mg). K. Saito

**1. Group separation of fission products with an -exchange resin in the oxalate form.** Seishi ıa, Eiji Shikata and Chizuko Yamaguchi ın Atomic Energy Res. Inst., Tokai, Ibaragi- *Japan Analyst*, 1958, **7** (11), 721.—When l fission products (aged for 3 years) in 0·5% Cl soln. (pH 6, 20 ml) are passed through a ın (diam. 6 mm, length 10 cm) of Dowex 5 (50 to 100 mesh), $^{137}Cs$ and $^{90}Sr$ pass through ut being adsorbed. Rare-earth elements $^{144}Ce$, $^{147}Pm$), $^{95}Zr$, $^{95}Nb$ and $^{106}Ru$ are eluted is order from the resin phase with 0·2 *N*, , 1 *N* HCl and 2 *N* $HNO_3$, respectively. K. Saito

**2. Titrimetric analysis of white metals.** L. J. ıdorfer (Inst. of Inorg. and Anal. Chem., Univ. echnol., Vienna, Austria). *Chemist Analyst*, **47** (4), 96–101.—Dissolve the sample (0·5 g) nc. HCl (10 ml) and conc. $HNO_3$ (2 ml), ling unnecessary heating. Add 25 ml of 4% KCl soln. and 25 ml of 0·2 *M* EDTA (disodium boil gently for 1 min., cool, and dilute to 250 *Procedure for total Sn and Pb*—Transfer an ot (25 ml) to a 250-ml conical flask, add satd. ıiourea soln. till the blue colour due to copper is ıarged, add 0·5 ml in excess, then add 15 ml of aq. hexamine soln., dilute to 150 ml, and back- te the excess of EDTA with 0·05 *M* $Pb(NO_3)_2$ red end-point with xylenol orange. *Procedure n*—To the soln. from the first titration add 2 g aF. Tin is thus freed from its EDTA complex, the EDTA so liberated is titrated with 0·05 *M* $NO_3)_2$, the end-point being a red colour which is e for 1 min. *Procedure for total Sn, Pb and Cu* a second aliquot (25 ml) add 15 ml of 30% aq. mine soln., dilute to 150 ml, and back-titrate excess of EDTA with standard Pb soln. as ribed above. *Procedure for Sb*—Dissolve a sample of the metal (0·5 g) in 10 to 15 ml of $H_2SO_4$ with heating, continue heating to ng and fume for 2 min. in the open beaker to ve $SO_2$. Cool, add successively 20 ml of water, l of conc. HCl and 100 ml of hot water, and te the Sb with 0·1 *N* $KBrO_3$ at 70°, with methyl ge as indicator, the end-point, which should be oached slowly, being the discharge of the pink ır. The suspended $PbSO_4$ does not interfere. lts for three alloys of known composition show factory recoveries. R. E. Essery

**3. Determination of water by titration with metrically generated Karl Fischer reagent.** Meyer, jun., and C. M. Boyd (Oak Ridge Nat. Tenn., U.S.A.). *Anal. Chem.*, 1959, **31** (2), 219.—Microgram amounts of $H_2O$ in organic nts, *e.g.*, glycols and strong amines, can be rmined by titration with Karl Fischer reagent ced by the electrolytic generation of iodine in n. of the depleted reagent in ethanediol. The oint is reached when an excess of iodine is ated, and is detected by the depolarisation of um indicator-electrodes. Assuming 100% nt efficiency, 1 mole of iodine is equiv. to de of $H_2O$ or 10·71 coulombs of generating t per mg of $H_2O$. Side reactions that con- iodine are eliminated by a supplementary ating current, adjusted to maintain the soln. end-point before the addition of the sample (1 ml). The more basic amines, *e.g.*, 1:2-diamino-propane, should be neutralised with a 15% w/v soln. of salicylic acid in ethanediol (instead of acetic acid in methanol) to reduce the rate of esterification. The procedure is applicable to concn. of $H_2O$ as low as 5 to 50 $\mu$g per ml, although the accuracy is higher for samples containing 500 to 1000 $\mu$g per ml (coeff. of variation $<2\%$). The sensitivity is $\simeq 2$ $\mu$g per ml. Limitations of the method are discussed; an advantage is the time saved by eliminating the preparation, standardisation, storage and measurement of the Karl Fischer reagent. W. J. Baker

**3394. Determination of traces of nickel in sodium metal.** T. M. Florence (Australian Atomic Energy Comm., Res. Estab., Sutherland, N.S.W.). *Anal. Chim. Acta*, 1958, **19** (6), 548–551.—The nickel-cyanide complex absorbs strongly at 268 m$\mu$; $Co^{2+}$, $Mo^{6+}$, $Cr^{6+}$ and $Cu^{2+}$ interfere. The sample is dissolved in abs. ethanol, acidified with a 5-ml excess of conc. HCl, evaporated to dryness and dried for 2 hr. at 120°. Dissolve the residue in the minimum of 0·1 *N* HCl and dilute to a known vol. Dilute an aliquot (5 to 75 $\mu$g of Ni) to 10 ml then add 1 drop of $HNO_3$ and boil; add 0·5 g of $NH_4Cl$ and 0·5 g of urea, boil till the pH has risen to 6 to 7, then simmer for 15 min. and filter. Wash the ppt. with 1% $NH_4Cl$ soln., add 5 drops of hydroxylamine hydrochloride soln. (10%) to the filtrate and boil. Cool, add 2·5 ml of KCN soln. (5%) and dilute to 25 ml. Read at 268 m$\mu$ against 0·5% KCN containing hydroxylamine hydrochloride. T. R. Andrew

**3395. Use of sulphuric acid to depress the interference of calcium in the determination of sodium with an EEL flame photometer.** R. D. Bond and J. T. Hutton (C.S.I.R.O., Div. of Soils, Adelaide, S. Australia). *Analyst*, 1958, **83**, 684–686.—In the relatively low-temp. coal gas - air flame of the EEL flame photometer all Ca salts are not volatilised to the same extent. Addition of phosphate has a depressive effect on the emission of Ca, but the effect is not constant and depends on the presence of other anions. Sulphate also depresses the Ca emission of $CaCl_2$ to a lower extent than $PO_4^{3-}$, but the depression is independent of other ions and is determined solely by the concn. of Ca. Quoted results of the effect of the addition of different amounts of $H_2SO_4$ to $CaCl_2$ soln. in the flame photometer with the "calcium" interference filter in position show that the Ca emission is progressively decreased until the $H_2SO_4$ added is equiv. to the Ca present. In the determination of Na in soln. containing Ca by means of the EEL flame photometer, $H_2SO_4$ should be added in an amount at least equiv. to the Ca present, and if the soln. contains anions such as $PO_4^{3-}$ or $HCO_3^-$ an additional amount of $H_2SO_4$ equiv. to any other metal ions present should be added. With a suitable filter, Ca emission can be determined and a correction can be applied to the Na value if, as often happens, the amount of Ca present is known. A. O. Jones

**3396. Rapid flame-photometric micro-determination of sodium, potassium and lithium in glass.** A. J. Hegedüs and M. Dvorszky (Forschungsinst. f. d. nachrichtentech. Ind., Tungsram, Budapest). *Mikrochim. Acta*, 1959, (1), 160–161.—The finely ground sample (20 to 50 mg) is evaporated to dryness with 1 ml of HF, dissolved in 10 drops of $HNO_3$ and re-evaporated to dryness. The residue is

dissolved in 2 ml of $HNO_3$ (10%) and diluted to 50 to 250 ml according to the expected content of alkali metal. Jena interference filters (SIF 589a, SIF 768a and SIF 670a) are used in the flame-photometric determination. T. R. ANDREW

3397. **Use of a flame photometer for the determination of sodium and potassium oxides in the routine control of glass compositions.** E. Walton and T. Robinson (Osram Glass Wks, Lemington, England). *J. Soc. Glass Tech.*, 1958, **42**, 271T–278T.—The sample (25 mg, 120 mesh) is decomposed with HF (1 ml) plus $HClO_4$ (10 drops); the mixture is evaporated to dryness and the residue is dissolved in warm HCl (1:4) (5 ml). The soln. is made up to 250 ml and an aliquot is taken for the determination of Na and K in an EEL flame photometer. After deducting the reagent blank, the percentages of $Na_2O$ and $K_2O$ are read from calibration curves, prepared from readings on soln. of a similar glass (made synthetically) covering a range of contents of $Na_2O$ and $K_2O$. Between different laboratories the results are reproducible to within 2% of the amount of oxide being determined. The method has been found to be particularly suitable for the furnace control of an "alkali-free" glass which actually contains $\simeq$0·25% of $Na_2O$ and 0·10% of $K_2O$.
W. J. BAKER

3398. **Determination of micron-sized particles. Detection of potassium ion.** B. J. Tufts (Cloud Physics Lab., Dept. of Meteorol., Univ. of Chicago, Ill., U.S.A.). *Anal. Chem.*, 1959, **31** (2), 242–243.—Airborne particles containing K may be detected and their size and number determined after reaction with sodium tetraphenylboron (1% aq. soln.). The air sample is drawn through a membrane filter, which is then floated on a few ml of the reagent soln. in a Petri dish, and washed by floating twice for 5 min. on water. After drying, the filter is mounted on a glass slide with immersion oil. The reaction sites are observed, as white granular spots, by microscopic examination under dark-ground illumination. The reaction sites may be counted and there is a definite ratio of particle size to size of reaction site. A ppt. with the reagent is formed by $NH_4^+$. This ion does not interfere under ordinary circumstances, as the ppt. forms only after exposure for 30 min. to the reagent soln. F. L. SELFE

3399. **Rapid analysis of gamma-emitters using gamma-ray scintillation spectrometer. II. Determination of caesium-137 in fission products.** Fumio Aoki, Seishi Yajima and Toshio Kurosawa (Gov. Chem. Ind. Res. Inst., Shibuya-ku, Tokyo). *Bull. Chem. Soc. Japan*, 1959, **32** (1), 42–45 (in English).—A simple and reliable analysis is achieved by combining the use of anion-exchange resins (Dowex 1-X7·5) in the oxalate and carbonate forms with measurement by a $\gamma$-ray scintillation spectrometer. Several similar aliquots are taken from the fission-products soln., to which are added various known amounts of pure $^{137}Cs$. The bulk of the uranium is extracted with tributyl phosphate - diethyl ether (1:1). The samples are then percolated through a mixed bed of the carbonate and oxalate forms of the resin. The alkali metals pass through. Each percolate is measured by using a $\gamma$-ray scintillation spectrometer, and the real peak height of the 0·66 MeV gamma is plotted against the amounts of added $^{137}Cs$ soln. The straight line is then determined by the method of least squares, and the amount of $^{137}Cs$ in the fission product is given by the length of the abscissa between intersection with the straight line and the orig
I. JONES

3400. **Potentiometric titration at constant curr of copper(II) in ammoniacal medium.** E. Nightingale, jun. (Sch. of Chem., Univ. of Min sota, Minneapolis, U.S.A.). *Anal. Chim. A* 1958, **19** (6), 587–592.—Cupric ions can be det mined with EDTA (disodium salt) in air-f ammoniacal medium by using the technique potentiometric titration at constant current (5 $\mu$ with a rotating platinum electrode - S.C.E. p Attempts to titrate with benzoin $\alpha$-oxime gave p results unless the ppt. was removed by centrifug or filtration after each addition of reagent.
T. R. ANDREW

3401. **Determination of oxygen in copper.** W. Harris and W. M. Hickam (Res. Lab., Westingho Electric Corp., Pittsburgh, Pa., U.S.A.). *A Chem.*, 1959, **31** (2), 281–283.—The sample (2 3 g) in a graphite boat is heated under high vacu to 1150°. Under these conditions, essentially only gas present is CO and the gas pressure can measured with a mercury manometer. The pressure is related to oxygen content by calibrati The method is simple and rapid in operation, time required for a determination being 15 m The standard deviation for a single determinat is $\pm$28 $\mu$g of O, so that the method is suitable refinery control. The method is not subject errors due to the presence of S in the copper. T theoretical basis for the non-interference of S discussed. The apparatus used is described a illustrated. F. L. SELF

3402. **Metallurgical polarographic analysis. Simultaneous determination of cadmium, nickel zinc in copper-base alloys.** Yoshiaki Miura (Yaw Iron and Steel Works, Fukuoka-ken). *Ja Analyst*, 1958, **7** (12), 783–785.—When Cu is pp as CuSCN, Cd, Ni and Zn remaining in the filtr can be simultaneously determined in a support electrolyte containing $NH_4Cl$ and aq. $NH_3$ so in the presence of $Na_2SO_3$ and gelatin. There is interference from $SCN^-$, $ClO_4^-$ or Na. The w of Co overlaps that of Zn and a large amount Mn interferes with the determination of Zn. *cedure*—Dissolve the sample (0·2 g) in aqua re (5 ml) and heat with $HClO_4$ (60%, 5 ml) to wh fumes. Cool, neutralise with 5 *N* NaOH, $HClO_4$ (5 *N*, 2 ml), saturated $Na_2SO_3$ soln. (1 *M* KSCN (10 ml) and water (50 ml) and boil 1 min. Cool, filter, wash the ppt. with 0·1% KS soln. containing 0·01% of $Na_2SO_3$ and make up filtrate and washings to 100 ml. Dilute an aliq to 50 ml with 2 *M* $NH_4Cl$ containing 2 *N* aq. (25 ml), saturated $Na_2SO_3$ soln. (2·5 ml) and gela soln. (1%, 0·5 ml) and record the polarogram.
K. SAIT

3403. **Determination of a trace of bismuth in silver. I. Co-precipitation with aluminium hy oxide.** Michihiro Ishibashi, Toyoshi Nagai, Tai Fujinaga and Wataru Funasaka (Fac. of Eng Kyoto Univ., Sakyo-ku, Kyoto). *Japan Ana* 1958, **7** (9), 553–556.—Aluminium hydroxide (2·7 of Al) can be used in place of Fe for the co-ppt Bi (0·00005 to 0·002%) and the Bi is polarogra cally determined in *N* $HNO_3$ containing 0·0 $Na_2SO_3$ and 0·01% gelatin. The recovery of decreases with increasing concn. of $NH_3$, pH

g the optimum for the pptn. of Al. The work-curve is linear for $<220$ μg of Bi per 25 ml of supporting electrolyte. The sample soln. is ed for 30 min. on a water bath with $Al(NO_3)_3$ . (0·1 *M*, 1 ml), $NH_4NO_3$ soln. (4 *M*, 5 ml) and $NH_3$ soln. (1·5 *M*) and then for 10 min. with a her addition of aq. $NH_3$ soln. (10 ml). The is filtered off, dissolved in 5 *N* $HNO_3$, re-pptd., olved in 5 *N* $HNO_3$, evaporated to dryness and olved in the supporting electrolyte (25 ml) for rography. K. Saito

404. **Spectrophotometric determination of traces old with Rhodamine B.** Hiroshi Inoshi (Gov. Res. Inst., Nagoya, Japan). *Mikrochim.* , 1959, (1), 9–17 (in English).—To 1 to 10 μg Au in 80 ml of 3 *N* HCl add 1·0 ml of $TeCl_4$ . (1 mg of Te per ml) and heat to boiling. Add essively 15 ml of satd. $SO_2$ soln., 10 ml of razine hydrochloride soln. (15%) and a further l of satd. $SO_2$ soln. Boil gently until the ppt. coagulated (5 to 15 min.) and set aside for 1 hr. er off the ppt. on a sintered glass filter (porosity nd wash it five times with 2 *N* HCl. Add 1 ml qua regia to the pptn. beaker, heat almost to ing and pour through the filter. Repeat with rther 1 ml and finally wash four times with er. Evaporate the aqua regia soln. and wash- to dryness, moisten with 1 drop of aqua regia set aside for 1 to 2 min. Add 2·5 ml of HCl *N*) and transfer to a separating-funnel with ml of water. Wash out the beaker into the nel with 5·0 ml of $NH_4Cl$ soln. (30%) and 10·5 of water. Mix, add 1·0 ml of Rhodamine B . Basic Violet 10) soln. (0·2%), mix, add 10·0 ml benzene and shake for 1 min., then transfer the zene layer to a centrifuge tube. Centrifuge 5 min. at 2000 r.p.m. and record the extinction he soln. against benzene in a 1-cm cell at 565 mμ hin 30 min. A calibration curve is prepared by rying out the colour formation as described above m the addition of 2·5 ml of 6 *N* HCl onwards) pure Au soln. Beer's law is obeyed up to 10 μg. e extinction of 10 μg of Au at 565 mμ is $\simeq 0{\cdot}6$ in -cm cell. Antimony, Ga, Fe, Pt and Tl do not erfere; 1 mg of Sn gives a colour equivalent to μg of Au. T. R. Andrew

405. **Separations involving sulphides. VIII. aration of ruthenium and indium from alkaline-th metals.** G. B. S. Salaria (Chem. Lab., Univ. Allahabad, India). *Anal. Chim. Acta*, 1959, **20** 68–69.—Ruthenium and In can be quant. arated from the alkaline-earth metals by thods similar to those described previously *al. Abstr.*, 1959, **6**, 2459). The sample soln. reated with aq. $NH_3$ until a turbidity appears then 2 *N* $Na_2S$, acetic acid and solid ammonium tate are added. After boiling and cooling the ture, the pptd. sulphide is filtered off, washed, d and weighed. Ruthenium is recovered with accuracy of $+0{\cdot}14$ to $-0{\cdot}33$% and In with an uracy of $+0{\cdot}29$ to $-0{\cdot}24$%.

**X. Separations of alkaline-earth metals from e elements that form thio salts.** I. K. Taimni S. N. Tandon (Chem. Lab., Univ. of Allahabad, ia). *Ibid.*, 1959, **20** (1), 70–72.—Arsenic, Sb, Se and Mo can be quant. separated from Ca, nd Mg by adding excess of 2 *N* $Na_2S$ and then lifying with HCl. After boiling and cooling mixture, the pptd. sulphide can be filtered off. ults are quoted for the analysis of a series of thetic mixtures. The method cannot be applied Sn because the ppt. of $SnS_2$ peptises on being lhed. W. T. Carter

3406. **Rapid determination of beryllium oxide in beryllium metal.** A. R. Eberle and M. W. Lerner (U. S. Atomic Energy Comm., New Brunswick Lab., N.J.). *Metallurgia, Manchr*, 1959, **59**, 49–52. —The method is based on that for the determination of oxide in aluminium. After selective dissolution of the metal in soln. of Br - methanol and HCl - methanol, BeO in the undissolved residue is analysed for Be by the conventional *p*-nitrophenyl-azo-orcinol method or, alternatively, by the addition of NaF and excess of 0·05 *N* $H_2SO_4$, followed by back-titration with 0·05 *N* NaOH. The method compares favourably with the HCl volatilisation procedure. J. W. O. Pyemont

3407. **Rapid radiometric determination of magnesium.** Atsushi Mizuike, Toshihiro Nakajima and Shizo Hirano (Inst. of Techno-anal. Chem., Fac. of Engng, Tokyo Univ., Hongo). *Japan Analyst*, 1958, **7** (9), 588–590.—Magnesium ($<20$ mg) is pptd. with $(NH_4)_2HPO_4$ labelled with $^{32}P$ and the radioactivity of the supernatant liquid is measured with a Geiger - Müller counter of the immersion type. Good agitation is essential for obtaining reproducible results. There is no interference from $<M$ $NH_4Cl$, $<200$ mg (per 60 ml) of NaCl, $<100$ mg of KCl and $<50$ mg of ammonium oxalate per 2 mg of Mg. K. Saito

3408. **Improved 8-hydroxyquinoline method for the determination of magnesium oxide in Portland cement.** H. A. Berman (Nat. Bur. of Standards, Washington, D.C., U.S.A.). *Bull. A.S.T.M.*, 1959, (237), 51–55.—The U.S. Federal and A.S.T.M. optional rapid volumetric methods (dissolution of Mg oxinate in hot HCl, addition of $KBrO_3$ - KBr and KI, followed by titration with $Na_2S_2O_3$) give high values, poor reproducibility and too many "specification" failures. Greater accuracy and reproducibility are attained by a double pptn. of Mg oxinate; the amount of oxine added is independent of the content of MgO, which had to be known approx. in the old method. The error is $\pm 0{\cdot}03$% for 2 to 5% of MgO; when determining lower concn. a known amount of MgO (as $MgCl_2$) is added to bring the concn. within the upper range. For cements high in $Mn_2O_3$, a preliminary removal of Mn is necessary. The improved procedure is recommended to replace the present referee method (determination as $Mg_2P_2O_7$). W. J. Baker

3409. **Detection of calcium ion.** H. Weisz (Inst. f. anorg. u. allg. Chem., Tech. Hochsch., Vienna). *Mikrochim. Acta*, 1959, (1), 32–35.— Calcium ions react with a soln. containing $Zr^{4+}$ and alizarin red S (**I**) which has been decolorised by addition of $F^-$, combining with $F^-$ and liberating $Zr^{4+}$ to react with **I**. Interference by $Ba^{2+}$ and $Sr^{2+}$ is overcome by their prior conversion into sulphates. *Procedure*—Dissolve 0·1 g of **I** in 100 ml of water and add 20 drops of $ZrO(NO_3)_2$ soln. (0·2%). Add dropwise NaF soln. (1%) till the red - violet colour is just discharged. The resulting soln. is stable. Treat the mixed carbonates, or an acetic acid soln., with 1 drop of $H_2SO_4$ (2 *N*) and evaporate to dryness. Cool, and add 1 drop of reagent soln. A red - violet colour within 1 to 3 min. indicates $Ca^{2+}$. As little as 1 μg of Ca has been detected. T. R. Andrew

3410. **The sucrose-extraction method of determining available calcium oxide in hydrated lime.** D. R. Moorehead and W. H. Taylor (Div. Building Res., C.S.I.R.O., Highett, Victoria, Australia).

*Bull. A.S.T.M.*, 1959, (236), 45–47.—The validity of the sucrose-extraction method for determining free CaO in hydrated and high-CaO limes is confirmed; satisfactory results are obtained in a fraction of the time required for a total analysis. The accuracy is unaffected by the amount of MgO present, but it does depend on the size of the sample. Optimum conditions for accuracy are—a sample of $\geq 0{\cdot}6$ g shaken for 15 min. in 10% sucrose soln. (100 ml) and then titrated with *N* HCl at 21°, followed by re-titration at the boiling-point to ensure complete hydrolysis of the sucrate.

W. J. Baker

3411. **Complexometric titration method for determining calcium in the presence of magnesium.** A. Ringbom, G. Pensar and E. Wänninen (Dept. of Anal. and Inorg. Chem., Åbo Akad., Finland). *Anal. Chim. Acta*, 1958, **19** (6), 525–531.—The 'conditional' formation constants for complexes of $Ca^{2+}$, $Mg^{2+}$ and $Zn^{2+}$ with 1:2-di-(2-aminoethoxy)-ethane-NN′-tetra-acetic acid (**I**) have been studied in the pH range 4 to 13, and that for the Zn - zincon complex in the range 6 to 13. The effect of varying the concn. of $NH_4^+$ is reported. It is shown that Ca may be titrated with **I** at pH 9·5 to 10·0 in the presence of Mg, with 2 ml of a soln. of the zinc salt of **I** (0·025 *M*) and 2 drops of 0·065% zincon in 0·002 *N* NaOH as indicator, in a borate buffer at an $NH_4^+$ concn. of 0·02 to 0·05 *M*.

T. R. Andrew

3412. **Flame-photometric determination of calcium in silicate rocks.** M. Stone and J. E. Thomas (Dept. of Geology, Univ. Coll., Keele, Staffs., England). *Analyst*, 1958, **83**, 691–694.—The powdered dried rock (0·2 g) is heated with HF and $H_2SO_4$ on a water bath until digestion is complete. The digest is heated to fuming, cooled, diluted with water and digested on the water bath for $\simeq$ 30 min. If insol. matter is present the liquid is then boiled and any remaining insol. matter is examined for Ca-containing minerals with a petrological microscope. The cooled soln. is adjusted to the yellow end-point of methyl red with dil. aq. $NH_3$, then centrifuged, and the supernatant liquid is decanted into a 50-ml flask (a double pptn. of $R_2O_3$ is usually necessary) and adjusted to the mark with 0·5 *N* $H_2SO_4$. The Ca content is then determined in the flame photometer with the zero set against 0·5 *N* $H_2SO_4$ and full-scale deflection with the appropriate standard soln. Quoted results indicate satisfactory accuracy.

A. O. Jones

3413. **Application of selective adsorbent resin to analytical chemistry. I. Separation and determination of calcium and magnesium in a concentrated solution of sodium chloride.** Toshiharu Takagi and Hiroshi Imoto (Toyo Soda Mfg Co., Tonda, Yamaguchi-ken). *Japan Analyst*, 1958, **7** (9), 565–568.—A special resin having a chelating action towards Mg and Ca was prepared from Amberlite IR-4B by the action of NaOH and chloroacetic acid (**I**). The rate of exchange between adsorbed Na and free Ca or Mg is very slow, and only the batch method can be used. By agitation for 30 min., both Ca and Mg ($<5$ mg) are quant. adsorbed by the resin (10 g) from NaCl ($<5$ *M*) and are eluted with 50 ml of 0·5 *N* HCl within 10 min. Interfering ions, including $Fe^{3+}$ and $Al^{3+}$, can be removed by extracting their oxinates with $CHCl_3$ from a neutral soln. (pH 7, adjusted with 5% $NaHCO_3$ soln.). *Procedure*—Treat Amberlite IR-4B (15·12 g) with NaOH soln. (9%, 1670 g) and **I** (150 g) at 60° to 70° for 17 hr.; wash and dry the product. Add thi resin (10 g) to the sample soln. and stir th suspension for 30 min. at room temp. Filter o the resin, wash with water and stir with HCl (0·5 N 50 ml) for 10 min. Filter the soln. into a measurin flask (250 ml) and use a 100-ml portion for th EDTA titration of Ca [2-hydroxy-1-(2-hydroxy-4 sulpho-1-naphthylazo)-3-naphthoic acid as indi cator] (*cf. Anal. Abstr.*, 1956, **3**, 2982) and of th sum of Ca and Mg (Eriochrome black T).

K. Saito

3414. **Complexometric determination of calciu and magnesium in cements.** D. Deur-Šiftar and E Bauman (Zavod za anorg. Tehnol. i Metalurg Zagreb, Yugoslavia). *Kem. i Ind., Zagreb*, 1959, (1), 1–7.—*Procedure*—A sample (1 g) of cement i boiled with 15 ml of $H_2O$ and 30 ml of conc. HC then cooled to 70° and treated with 1% gelatin soln added dropwise. The ppt. is filtered off after 1 min., then washed and ignited to give $SiO_2$. Th filtrate can be treated with bromine water and ac $NH_3$ for the pptn. of $Al(OH)_3$ and $Fe(OH)_3$, or the A and Fe can be masked with triethanolamine. Th filtrate is then made up to 500 ml and 50-ml al quots are taken for the determination of Ca and M with EDTA.

A. Grochowski

3415. **Rapid and accurate automatic titration c calcium and magnesium in dolomites and limestone Use of EDTA titrant and automatic derivativ spectrophotometric end-point determination.** H. V Malmstadt and T. P. Hadjiioannou (Dept. of Chem and Chem. Engng, Univ. of Illinois, Urbana, U.S.A. *Anal. Chim. Acta*, 1958, **19** (6), 563–569.—B utilising an automatic derivative spectrophoto metric titrimeter (*cf. Anal. Abstr.*, 1957, **4**, 4209 Ca may be determined in the presence of Mg b EDTA titration at pH 13, with calcon as indicato Total Mg plus Ca is determined at pH $\simeq$10 wit Eriochrome black T as indicator. Results ar reported in the ranges 0·2 mg to 2·0 mg for Mg an 1·0 to 4·0 mg for Ca. The time required for bot determinations is $<5$ min.

T. R. Andrew

3416. **Limestone for making colourless glasse** British Standards Institution (2 Park Street London). B.S. 3108: 1959, 15 pp.—Sampling meth ods are given, and apparatus and procedure specifie for the following determinations—moisture, size grading, inspection for magnetic materials an carbonaceous matter, qual. analysis, non-volatil matter insoluble in HCl, Al, Ca, Mg, iron oxide and organic matter.

H. M.

3417. **Detection of barium and strontium in a drop** H. Weisz (Inst. f. anorg. u. allg. Chem., Tech Hochsch., Vienna). *Mikrochim. Acta*, 1959, (1) 29–31.—The test drop is absorbed on filter-pape and treated with Na rhodizonate soln. (0·1%) A red - brown stain indicates Ba or Sr or both Wash twice with acetic acid (1:2) to remove exces of reagent, and add one drop of $AgNO_3$ soln. (1% and one drop of acetic acid (1:2). In the presenc of Sr a blue - violet fleck appears. A spot o ammonium oxalate soln. (2%) is added and th test spot is held over conc. aq. $NH_3$. The colour due to Ag and Sr rhodizonates and free rhodizoni acid disappear, while the red Ba rhodizonate i unaffected.

T. R. Andrew

3418. **Flame-photometric determination of sma amounts of barium.** M. Dzubay (Agric. Exp Inst., Délalföld, Szeged, Hungary). *Magyar Kém*

v., 1958, **64** (12), 483–484.—The determination Ba in 0·01 to 0·001 *M* $BaCl_2$ soln. at 770 mμ, in presence of large amounts of Ca, is described. both Ca and Mg give a slight emission at this relength, the sample and standard soln. are usted to contain 2·5% of $CaCl_2.2H_2O$ and of $Cl_2.2H_2O$. The coeff. of variation for 9 measure-nts is ±0·72% and for a single measurement is 2·05%. G. Szabo

419. **Decomposition of barium sulphate with rogen chloride and determination of the ium by titration of the chloride formed.** J. erdenbos, Y. C. de Wijs and J. E. Ordelman iv. of Amsterdam, Holland). *Z. anal. Chem.*, 9, **165** (6), 421–423.—Barium sulphate is quant. omposed by heating at 1000° in HCl gas, and Ba can be indirectly measured by potentio-ric titration, with $AgNO_3$, of the chloride formed. alysis of 6 standards showed a mean decomposi-n of 100% with a standard deviation of ±0·9%. 1100°, recovery of $Cl^-$ is low owing to its volatility this temp. The method is often applicable to ure $BaSO_4$. G. P. Cook

420. **Separation of strontium-90 and yttrium-90 the use of an anion-exchange resin in the oxalate m.** Seishi Yajima, Eiji Shikata and Chizuko maguchi (Japan Atomic Energy Res. Inst., kai, Ibaragi-ken). *Japan Analyst*, 1958, **7** (11), .—Carrier-free $^{90}Sr$ in 1% ammonium oxalate n. of pH 2 to 7 passes through a column (diam. m, length 10 cm) of Dowex 1-X7·5 (50 to 100 sh) (oxalate form), but $^{90}Y$ is adsorbed and can eluted with 0·5 *N* HCl. A similar result was ained by the use of 0·5% $NH_4Cl$ soln. (pH 2 to 6) place of the oxalate soln. K. Saito

421. **Electrochromatography in the separation of s. VI. Separations of zinc-group metals.** A. K. jumdar and B. R. Singh (Jadavpur Univ., cutta, India). *Anal. Chim. Acta*, 1958, **19** (6), –522.—In KCN soln., at pH 6, a quaternary xture of Ni, Zn, Co and Mn may be resolved by ctrochromatography. No success was obtained h quaternary mixtures in 30 other electrolytes died. T. R. Andrew

422. **Determination of cadmium in zinc anodes.** C. G. Wheeler and D. Durant (Central Dockyard ., H. M. Dockyard, Portsmouth, England). *tallurgia, Manchr*, 1959, **59**, 53–54.—Cadmium h some Zn is removed as sulphide from the $H_2SO_4$ n. The Zn is separated with an $NH_4Cl$ - phos-te soln. and the Cd finally determined colori-rically as the sulphide. J. W. O. Pyemont

423. **Extraction and flame-spectrophotometric ermination of aluminium.** H. C. Eshelman, J. A. n, O. Menis and T. C. Rains (Dept. of Chem., v. of Tennessee, Knoxville, U.S.A.). *Anal. m.*, 1959, **31** (2), 183–187.—Selective extraction n a chelating agent (2-thenoyltrifluoroacetone or fferron) in 4-methylpentan-2-one can be used to ate Al from many elements. The organic se can then be aspirated directly into an oxy-ylene or oxy-hydrogen flame with a 100-fold ease in sensitivity compared with a similar soln. The calibration curve is linear from 5 to g of Al per ml. The effect of a wide variety of has been studied. Procedures for the pre-nary separation from large amounts of inter-g elements are outlined. K. A. Proctor

3424. **Colorimetric determination of aluminium in heat-resistant alloys.** H. Zibulsky, M. F. Slowinski and J. A. White (Austenal Inc., Dover, N.J., U.S.A.). *Anal. Chem.*, 1959, **31** (2), 280–281.—After dissolution of the alloy, a double cupferron - $CHCl_3$ separation leaves Al in the aq. phase. Complexing agents are added, followed by 8-hydroxyquinoline and the aluminium 8-hydroxyquinolinate formed is extracted with $CHCl_3$. Three extractions are necessary. The extracts are made up to 100 ml and the extinction of the soln. is measured at 380 mμ or 425 mμ against a reagent blank. Satisfactory results are claimed for steels and nickel-base alloys containing up to 7% of Al. In the suggested procedure, only U, Mg, Mn and rare-earth elements cause serious interference. F. L. Selfe

3425. **Photometric determination of aluminium and titanium in polyethylene.** W. T. Bolleter (Monsanto Chem. Co., Texas City, U.S.A.). *Anal. Chem.*, 1959, **31** (2), 201–203.—Wet- and dry-ashing procedures for the decomposition of polyethylene samples are described. The soln. obtained by either procedure is diluted to 100 ml and separate aliquots are taken for the Al and Ti determinations. *Procedure for aluminium*—The aliquot is treated to give aluminium 8-hydroxyquinolinate, and the complex is extracted into 10 ml of trichloroethylene. The extinction of the extract is measured at 390 mμ against a reagent blank. The optimum concn. range is from 5 to 30 μg of Al per 10 ml of solvent for a 1-cm cell. The system conforms to Beer's law over this range, and Al can be determined to within ±0·2 μg. Results are quoted for the extent of interference by Ti, V, Zr, Fe, Mo, Ni, Cu, Zn and Cr. *Procedure for titanium*—The aliquot is treated to give the coloured Ti complex with chromotropic acid, adding EDTA (disodium salt) to remove the green iron - chromotropic acid complex. The extinction of the soln. is measured at 420 mμ against a reagent blank. The optimum concn. range in the final soln. is 0·4 to 2·5 p.p.m. for a 1-cm, and 0·08 to 0·5 p.p.m. for a 5-cm, cell. Results are quoted for the extent of interference due to Zr, Cr, Fe, V, Cu, Mo, Ni, Zn, Al and $NH_4^+$. The standard deviation for the determination of each metal is ±1 in the range 5 to 50 p.p.m. F. L. Selfe

3426. **Volumetric determination of aluminium and ferric iron with EDTA with the use of Chrome azurol S and o-dianisidine as indicators.** Tsutomu Matsuo (Fac. of Liberal Arts and Sci., Univ., Koshirakawa-cho, Yamagata). *Japan Analyst*, 1958, **7** (9), 557–560.—The indication of the end-point for the EDTA titration of $Al^{3+}$ at pH 4 (phthalate buffer) with Chrome azurol S (C. I. Mordant Blue 29) (**I**) is not sharp. Ferric iron is satisfactorily titrated at pH 4 with *o*-dianisidine or at pH 2 with **I** as indicator. Differential titration (indicator **I**) at pH 2·0 (for Fe) and 4·0 (for Al) always gives low values for Al. K. Saito

3427. **Metallurgical polarographic analysis. V. Rapid determination of copper and iron in aluminium and its alloys.** Yoshiaki Miura (Yawata Iron and Steel Works, Fukuoka-ken). *Japan Analyst*, 1958, **7** (11), 699–702.—*Procedure*—Dissolve the sample (0·5 g) in NaOH (5 *N*, 20 ml), add warm water (80 ml) and $Na_2S$ soln. (20%, 5 ml) and warm at 50° for 30 min. Filter off the ppt., wash with 2% $Na_2S$ soln. and dissolve the residue in $HNO_3$ (1:1, 10 ml) and aq. bromine soln. (a few ml). Evaporate to <5 ml, neutralise with 5 *N* NaOH and add ethylenediamine tartrate soln. (2 *M*, 12·5 ml),

$K_4P_2O_7$ soln. (1 *M*, 5 ml) and water to a total vol. of 50 ml. Measure the limiting current at −0·35 V (for Cu) and −0·60 V (for Fe) *vs.* the S.C.E. The results agree well with those obtained by conventional methods and the time taken for a determination is <90 min. K. Saito

3428. **Fluorimetric determination of gallium with Eriochrome red B.** Yasuharu Nishikawa (Chem. Dept., Fac. of Sci., Kyoto Univ., Sakyo-ku). *Japan Analyst*, 1958, **7** (9), 549–552.—The fluorimetric detection of Ga (*cf.* Wiebush, *Anal. Abstr.*, 1956, **3**, 2961) was applied to its quant. determination. The intensity of the fluorescence (max. 490 mμ) is strongest at pH 3 to 3·9; it increases in the presence of ammonium acetate soln. (optimum 10%, 2 ml per 50 ml) and remains unchanged for 2 hr. The working curve is linear for <10 μg of Ga per 50 ml. Interference resulting from $Fe^{III}$, $Tl^{III}$, $VO_3^-$, $WO_4^{2-}$ and $MoO_4^{2-}$ is masked with hydroxyammonium chloride; Al, Cu and Th give similar colorations; Ga is separated by extraction with diethyl ether. The sample soln. is mixed with Eriochrome red B (C. I. Mordant Red 9) soln. (0·1%, 0·4 ml) and ammonium acetate soln. (10%, 2 ml), the pH is adjusted to 3·2 with *N* $H_2SO_4$, the whole is diluted to 50 ml and heated on a water bath for 10 min. The fluorescence is measured with quinine sulphate (0·08 μg per ml of *N* $H_2SO_4$) as standard. K. Saito

3429. **Complexometric titration of gallium with fluorescent indicator.** R. H. A. Crawley (B.T.-H. Res. Lab., Rugby, England). *Anal. Chim. Acta*, 1958, **19** (6), 540–541.—Evaporate the gallium soln. to about 5 ml, add 5 ml of K H phthalate soln. (4%) and adjust the pH to 2·5 to 3·5. Add 1 ml of hydroxyammonium chloride soln. (20%) and 1 ml of 8-hydroxyquinoline soln. (0·05% in 0·5% acetic acid) and titrate with 0·001 *M* EDTA (disodium salt); u.v. irradiation is used to detect the end-point (disappearance of fluorescence). The range is 50 to 1000 μg of Ga; for amounts of <50 μg, errors were too large for the method to be of practical use. T. R. Andrew

3430. **Determination of thallium by a dithizone mixed-colour method.** R. S. Clarke, jun., and F. Cuttitta (U.S. Geological Survey, Washington, D.C.). *Anal. Chim. Acta*, 1958, **19** (6), 555–562.—Thallium is extracted by a $CHCl_3$ soln. of diphenylthiocarbazone (**I**) (0·008%) (15 ml) from a soln. containing Na citrate (5 ml of 25% soln.), $Na_2SO_3$ (1 ml of 5% soln.) and KCN (2 ml of 5% soln.) in a total vol. of 20 ml. The extract [together with washings with $CHCl_3$ (2 × 3 ml)] is shaken with $HNO_3$ (15 ml of 0·08 *N*). The aq. layer is retained and neutralised to methyl red with NaOH soln. (0·08 *N*); KCN (2 ml of 5% soln.) is added, followed by **I** soln. (15 ml of 0·0027% in $CHCl_3$) and the $CHCl_3$ extract is measured at 505 mμ against pure $CHCl_3$. The range is up to 100 μg of Tl; Pb, Bi and $Sn^{II}$ interfere. T. R. Andrew

3431. **EDTA titration of micro quantities of rare earths.** K. L. Cheng (Metals Div., Kelsey Hayes Co., Utica, N.Y., U.S.A.). *Chemist Analyst*, 1958, **47** (4), 93–94.—The method has been used for the indirect titration of all the rare-earth metals (except radioactive Pm) in the tervalent state, in the pH range 4 to 10, with 1-(2-pyridylazo)-2-naphthol as indicator. To a 15- or 25-ml porcelain dish add a suitable aliquot of 0·001 *M* rare-earth-metal soln., a slight excess of 0·001 *M* EDTA and a few crystals of sodium or ammonium acetate. Adjust to pH between 4 and 10 with acetic acid or aq. NH add 1 to 2 drops of 0·1% methanolic indicator soln and 2 to 3 ml of methanol, and back-titrate th excess of EDTA with 0·001 *M* $CuSO_4$ till th colour changes from yellow to reddish brown Correct the result by a reagent blank. Diethylene triaminepenta-acetic acid is as satisfactory as EDT. for this titration. The pH should be above 3, bu as low as feasible, to attain higher selectivity. A pH 5 to 6, $Ce^{IV}$ cannot be titrated satisfactorily but it can be reduced to $Ce^{III}$ with ascorbic acid when the titration is satisfactory at pH 5 to 10 the excess of ascorbic acid does not interfere. Cup ferron is not satisfactory as a masking agent in th titration of mixtures of rare-earth metals, as a excess interferes with the end-point. R. E. Essery

3432. **Rapid analytical methods for metals an minerals. VII. Polarographic determination o cerium in alloys and minerals.** J. Doležal an J. Novák (Inst. Anal. Chem., Charles' Univ Prague). *Chem. Listy*, 1958, **52** (11), 2060–2065.— Results obtained in studying the polarographi behaviour of Ce in soln. of $K_2CO_3$ and K Na tartrat (*Chem. Listy*, 1958, **52**, 582) have been applied t the determination of Ce in various materials. Th method is suitable for the determination of 1% o Ce in iron and zinc, 3% in aluminium, 5% i vanadium and nickel, 0·1% in thorium and uran ium, 0·5% in yttrium, and 5% in scandium; th presence of large amounts of Bi, $Cr^{3+}$, Ti, Pb, Co Mg, Mo, W, Pr, Nd, Sm, Gd and Er causes no inter ference. *Procedure for alloys containing Th, Al an Mg*—Dissolve the sample containing about 5% o Ce (0·5 to 1 g) in a mixture of $HNO_3$, HCl an $H_2O$ (3:1:6) (20 ml) by heating in a porcelain dish evaporate to dryness, add $HNO_3$ (1:2) (1 ml) an $H_2O$ (30 ml) and heat till dissolution is complete Transfer the soln. to a 100-ml flask, mix, make up t volume and transfer 5 ml to a 25-ml flask. Remov O by bubbling with N (5 min.), add saturated soln of K Na tartrate (5 ml) and $K_2CO_3$ (8 ml), mix make up to volume, transfer immediately to polarographic vessel, remove O by bubbling with N for 5 min. and record the wave from +0·1 V *vs* the S.C.E. Evaluate the results by the metho of standard additions. *Procedure for Ce in monazit* —Fuse the finely powdered sample (0·5 g) wit $Na_2O_2$ (5 g), cool and dissolve in $H_2O$. Filter o the pptd. hydroxides on paper, wash with 0·1 *N* KOH, ignite and fuse the residue with NaOH (0·5 to 1 g). Cool, add $Na_2O_2$ (5 to 8 g), repea the fusion and filtration, wash with 0·1 *N* KOH (20 ml), take up the ppt. in $HNO_3$ (1:4) (20 ml) filter, add to the filtrate $H_2O_2$ (30%) (3 drops and heat till the yellow colour is discharged Transfer to a 100-ml flask, add *M* KOH till a ppt. o hydroxides is formed, add conc. $HNO_3$ (5 drops and dilute with $H_2O$ to vol. Take 5 ml of this soln and proceed as described above. J. Zýka

3433. **The separation of fission products. II Separation of carrier-free praseodymium-144 b extraction from cerium-144.** Masuo Yagi (Fac. o Educ., Shizuoka Univ., Oiwa-cho). *Japan Analyst* 1958, **7** (12), 775–778.—Cerium-144, pptd. wit carrier Ce as iodate by the usual method, is mixe with glass wool and placed in an ice-cooled colum (diam. 10 mm, height 15 mm). When this colum is eluted with $HNO_3$, $^{144}Pr$ is eluted together wi Ce and the amount of Ce increases with increase concn. of $HNO_3$. However, by the use of conc

·005 *N* (rate of flow, 3 ml per min.), the amount Ce eluted is negligible; the radiochemical purity is 7%. K. Saito

3434. **Extraction and flame-spectrophotometric ermination of lanthanum.** O. Menis, T. C. Rains l J. A. Dean (Anal. Chem. Div., Oak Ridge Nat. ., Tenn., U.S.A.). *Anal. Chem.*, 1959, **31** (2), –191.—Lanthanum can be selectively extracted h 2-thenoyltrifluoroacetone in 4-methylpentan- ne from a buffered solution (pH 5) and then ermined by flame photometry. Of several ission bands, that at 743 mμ is the most suitable measurement. The effect of a number of inter- ng elements has been studied: of these only Ti l Al interfere when they are present in greater ounts than the La. Fluoride and phosphate erfere by preventing the extraction of the La. K. A. Proctor

3435. **Suppression of cyanogen bands for the ctrographic analysis of erbium oxide.** E. M. mmaker, G. W. Pope, Y. G. Ishida and W. F. agner (Dept. of Chem., Univ. of Kentucky, xington, U.S.A.). *Appl. Spectroscopy*, 1958, **12** , 161–163.—The suppression of cyanogen bands m d.c. arc spectra by using atmospheres of A, and $CO_2$ with or without O has been investigated. orking curves for the determination of Dy, Tm l Ho in erbium oxide have been prepared from ectra of samples arced in an atmosphere of 80% of and 20% of O. Cyanogen bands were eliminated l the background intensity reduced so that sitive lines could be used for the determination. K. A. Proctor

3436. **Photometric determination of silicon as nolybdosilicic acid.** A. Ringbom, P. E. Ahlers l S. Siitonen (Dept. of Anal. and Inorg. Chem., o Akad., Finland). *Anal. Chim. Acta*, 1959, (1), 78–83.—The observations of Strickland *Amer. Chem. Soc.*, 1952, **74**, 862, 868, 872) on e formation of α- and β-molybdosilicic acids have en utilised to develop an accurate colorimetric thod for silicon in rocks and other silicate terials. *Procedure*—Fuse the sample (0·1 to g) containing up to 70% of $SiO_2$ with NaOH g) in a nickel crucible. Dissolve the melt in ter containing 0·05 *M* EDTA (disodium salt) ml) and dilute to 500 ml. Pipette a suitable quot into a flask containing ammonium molyb- te soln. [35·3 g of $(NH_4)_6Mo_7O_{24}.4H_2O$ per litre] ml) and sufficient chloroacetic acid - ammonium oroacetate buffer to give a pH of 3·0 to 3·7. at in boiling water for 5 to 10 min., dilute to ml and measure the extinction at 390 mμ. e effects of pH, concn. of molybdate and the erference caused by P, Ge and As have been died. Results are given for a series of standard mples. W. T. Carter

3437. **Simple determination of silicon as a non- allic inclusion in weld metal.** Shuichiro Mizo- hi and Tadaji Oguma (Toyo Denkyoku Kogyo , Hiratsuka-cho, Shinagawa-ku, Tokyo). *Japan alyst*, 1958, **7** (9), 586–587.—The amount of Si on-metallic inclusion is determined by deducting Si content measured by the colorimetric method m that by the gravimetric. The results agree with those by the electrolytic method. K. Saito

3438. **Polarographic determination of tin in the pre- ce of dichromic acid.** J. Šára (Res. Inst. Electro- . Physics, Prague). *Chem. Průmysl*, 1958, **8** (12), 636–637.—Citric acid has been found to be the most suitable agent for the reduction of dichromic acid (**I**) and for the removal of its interfering influence in the polarographic determination of Sn in the presence of **I** as well as of other oxidising agents (peroxide, bromate, persulphate, permanganate). The total amount of Sn can be determined whatever its valency. *Procedure*—To 5 ml of the soln., containing $>1$ millimole of Sn in 1 ml, add 5 ml of a soln. of citric acid (**II**) (52·5 g of **II**, 53·5 g of $NH_4Cl$ and 154 ml of conc. HCl, diluted to 250 ml), heat till green or blue - green, and cool. Add gelatin soln. (0·1%) (3 drops) and dilute to 50 ml with a soln. of 4 *N* $NH_4Cl$ which is *N* in HCl. Transfer to a polarographic vessel, remove O with N and register the wave from $-0·2$ to $-0·8$ V. Evaluate by the method of standard additions. Measure the height of the wave at $-0·56$ V. If As, Sb, Pb, Cu or Bi is present, the soln. is oxidised with $KMnO_4$ and determined after reduction with **II**. Results are precise to within ±3%. J. Zýka

3439. **Metallurgical polarographic analysis. VI. Rapid determination of tin(IV) and lead. Analysis of solders.** Yoshiaki Miura (Yawata Iron and Steel Works, Fukuoka-ken). *Japan Analyst*, 1958, **7** (12), 779–782.—By using 4 *M* $NH_4Br$ as supporting electrolyte (Lingane *et al.*, *J. Amer. Chem. Soc.*, 1945, **67**, 919), $Sn^{IV}$ gives two waves at $-0·22$ and $-0·56$ V *vs.* the S.C.E., the second overlapping the Pb wave at $-0·56$ V. The amount of Sn is determined from the height of the first wave and that of Pb calculated from the height of the second wave. There is no interference from HCl ($<1$ *N*), Cd, As, Zn, and small amounts of Cu, Fe, Bi and Sb. The results agree with those obtained by conventional methods and the time taken for a determination is $<40$ min. K. Saito

3440. **Ultra-violet spectrophotometric determination of lead with perchloric acid.** Masayoshi Ishibashi, Yuroku Yamamoto and Kazuo Hiiro (Chem. Dept., Kyoto Univ., Sakyo-ku). *Japan Analyst*, 1958, **7** (9), 582–585.—Lead perchlorate exhibits an absorption at 208 mμ at pH $<3·4$ and the extinction is proportional to the amount of Pb ($<20$ p.p.m.) at a given pH; in alkaline soln. the absorption at 208 mμ disappears and another one appears at 240 mμ, the extinction markedly changing with time. Ferric iron ($>1$ p.p.m. for 10 p.p.m. of Pb), $Sn^{4+}$ ($>20$ p.p.m.), $Sb^{5+}$ and Bi give similar colorations and interfere. The range for colorimetry is increased by the use of a differential method with *N* $HClO_4$ containing 40 p.p.m. of Pb as reference, and by measuring the extinction at 218 mμ. K. Saito

3441. **Determination of bivalent and tervalent titanium in chloride melts by means of ferric chloride.** L. E. Ivanovskiĭ, N. A. Loginov and M. V. Smirnov (Inst. Chem., Ural Branch of Acad. Sci. USSR, Sverdlovsk). *Zhur. Anal. Khim.*, 1958, **13** (6), 671–673.—Cool a suitable sample in an inert atmosphere (argon) and transfer it into a test-tube fitted with a side arm. Introduce into the side-arm enough previously prepared $KFeCl_4$ (pure $FeCl_3$ fused at 450° to 500° with a eutectic mixture of KCl and LiCl in a current of Cl) for the complete oxidation of $Ti^{2+}$ and $Ti^{3+}$ to $Ti^{4+}$. Fill the tube with pure argon and place the lower part, containing the sample, in a hot oven. The side-arm must be in a cold zone outside the oven. When the sample has melted, tilt the tube so that $KFeCl_4$

is introduced into the melt. Shake vigorously, remove the tube from the oven and cool it as soon as possible to room temp. Weigh the sample, dissolve it in dil. (10%) $H_2SO_4$ or HCl and determine $Fe^{II}$. Take another sample melt and, after cooling it to room temp. in an inert atmosphere (argon), dissolve it in dil. (10%) $H_2SO_4$ or HCl and determine $Ti^{III}$. If $n$ = milli-equiv. of $Fe^{2+}$ for 1 g of sample fused with $FeCl_3$, and $m$ = milli-equiv. of $Ti^{3+}$ for 1 g of sample in aq. soln., then the analysed salt melt contains $11{\cdot}88\ (n - m)$ % (w/w) of $TiCl_2$ and $15{\cdot}43\ (2m - n)$ % (w/w) of $TiCl_3$.

W. Roubo

3442. **Rapid determination of chlorine in titanium.** Nakaaki Oda and Masaji Kubo (Takaoka Plant, Nippon Soda Co., Toyama-ken). *Japan Analyst*, 1958, **7** (11), 707–711.—Various methods for the determination of Cl in metallic titanium were examined for their suitability in routine analysis. No loss of Cl takes place when $<30$ ml of HF (46%) is used for 5 g of the sample (20 to 30 mesh) containing $\simeq 0{\cdot}05\%$ of Cl. Other conditions, including the amount of $HNO_3$ (oxidant for Ti) and $AgNO_3$ and the time for digestion of AgCl, were also examined. The error is $\simeq 5\%$ for $>0{\cdot}05\%$ of Cl. *Procedure*—Dissolve the sample (5 g) in HF (46%, 20 ml in 3 portions) add $H_3BO_3$ soln. (10%, 50 ml) and $HNO_3$ (20 ml) and stir until the soln. becomes colourless. Filter, if necessary, and add $AgNO_3$ soln. (5%, 10 ml) and centrifuge (3000 r.p.m.) for 10 min. Keep the product in the dark for 30 min. and filter off the ppt. on asbestos, wash with 1% $HNO_3$ and water and dry at 130° in a current of filtered air.

K. Saito

3443. **Analytical aspects of some organic acids. I. Gravimetric determination of zirconium by o-phenylenedioxydiacetic acid.** C. S. Pande and T. S. Srivastava (Chem. Dept., Univ., Lucknow, India). *Z. anal. Chem.*, 1959, **165** (1), 11–16 (in English).—Zirconium ($>2$ mg) is quant. pptd. from 0·1 to 0·4 $N$ HCl by *o*-phenylenedioxydiacetic acid (**I**). The ppt. is of variable composition and must be ignited to $ZrO_2$ before weighing. In the determination of 42 mg of $ZrO_2$, Ca (296 mg), Ba (375), Zn (161), $Hg^{2+}$ (373), Al (213), Ce (167), Ti (137), Th (187), $UO_2^{2+}$ (206), $Mn^{2+}$ (164), $Fe^{3+}$ (283), Co (326) and Ni (324) do not interfere. Contamination of the ppt. by $V_2O_4^{4+}$ (162 mg) and $Cr^{3+}$ (139 mg) is eliminated by double pptn.; $SO_4^{2-}$ (threefold excess) do not interfere. Results for the determination of 42 mg of $ZrO_2$ are accurate to within $\pm 0{\cdot}5\%$. *Procedure*—To a boiling aliquot (2 to 100 mg of Zr) add $NH_4NO_3$ (5 g per 100 ml) and, slowly with stirring, hot 2% aq. **I**. Adjust the acidity of the soln. to 0·3 $N$ in HCl. Collect the ppt., wash it with hot 0·1% **I** soln., and ignite to $ZrO_2$.

J. P. Stern

3444. **Volumetric determination of zirconium. I. Titration in alkaline medium with potassium permanganate.** A. Schneer and H. Hartmann (Dept. of Gen. and Inorg. Chem., L. Eötvös Univ., Budapest). *Magyar Kém. Foly.*, 1959, **65** (1), 31–36.—A method has been developed for the determination of mandelic acid (**I**) and *p*-bromomandelic acid with $KMnO_4$ in alkaline medium, and is applied to the determination of Zr. *Procedure*—Concentrate the HCl soln., containing Zr (2 to 20 mg) and any other cation, to 20 to 100 ml, depending on the total concn. Add conc. HCl (15 to 80 ml) and precipitate Zr at 95° by adding dropwise, with stirring, a 16% soln. of **I** (15 to 80 ml). Heat the mixture on a water bath for a few hours, with occasional stirring, and then set aside at room temp overnight. (If 0·2 to 0·4 mg of Zr is present, kee for 2 days and, if $\simeq 0{\cdot}1$ mg of Zr is present, keep fo 3 days.) Collect the Zr tetramandelate on a 10G glass filter and wash with the mother liquor of soln. from which the only cation, Zr, has bee pptd. with **I**. Transfer the last traces of the ppt to the filter with ethanol, wash with ethanc (3 × 10 ml) and diethyl ether (2 × 10 ml) and dry Dissolve the ppt., with suction, at $\simeq 60°$ with 5 $N$ to 6 $N$ $Na_2CO_3$ (4 × 5 ml) and wash the filter wit $H_2O$ (10 to 15 ml). Add 23% (w/w) NaOH soln (10 ml) and 0·5 $N$ $KMnO_4$ (20 ml). After 10 min. add $H_2O$ (250 to 300 ml), $\simeq 50\%$ (w/w) $H_2SO_4$ (2 ml) and 0·5 $N$ oxalic acid (**II**). Warm the soln. t 60° and back-titrate the excess of **II** with 0·1 $N$ $KMnO_4$. Carry out a blank; the difference betwee the two $KMnO_4$ titrations gives the wt. of Z present. It was found that 1 ml of 0·1 $N$ KMnO $\equiv 0{\cdot}5136$ mg of Zr. The error is $<\pm 1\%$.

A. G. Peto

3445. **Analytical chemistry of zirconium. I Solochrome violet R as indicator for the micro- an macro-titration of zirconium with EDTA.** J Korkisch and A. Farag (II Chem. Inst., Vienna Univ., Austria). *Z. anal. Chem.*, 1959, **165** (1), 6–10 —Solochrome violet R (C. I. Mordant Violet 5 forms a red - violet complex with Zr in hot $N$ HC and is useful as an indicator for the titration of Z with EDTA. The accuracy for 1·0 to 10 mg an 10 to 50 mg of Zr in 25 ml is within $\pm 1{\cdot}0$ an $\pm 0{\cdot}2\%$, respectively, and for 10 to 1000 $\mu$g o Zr in 10 ml, by micro-titration, within $\pm 1{\cdot}0$ $\mu$g Large amounts of $Sn^{2+}$, $Fe^{3+}$ or $V^{5+}$ affect the indi cator, and coloured ions (Cu, $Cr^{3+}$, Co and Ni affect the end-point; Mo, W and $Ti^{4+}$ form complexe with the indicator and interfere, as do $PO_4^{3-}$ an $F^-$. Interference by $F^-$ is eliminated by the addi tion of 2·5% $ThCl_4$ soln. in $N$ HCl. *Procedure*— Adjust the soln. of Zr with HCl until it is 1 $N$ an heat in boiling water (1 to 2 min.). In the presenc of $Fe^{3+}$ add 0·1% $SnCl_2$ soln. dropwise until the Fe is completely reduced. Add a 0·1% soln. of indi cator (0·5 ml per 10 ml) and heat for 1 min. Titrat with EDTA soln. (disodium salt) to the orange end point and correct the result by a blank.

J. P. Stern

3446. **Rapid determination of zirconium in ferro-zirconium by EDTA titration.** Shigeo Wakamatsu (Toto Seiko Co., Minami-sunamachi, Koto-ku Tokyo). *Japan Analyst*, 1958, **7** (9), 578–581.—For the back-titration of the excess of EDTA with $Cu^{2+}$ in the presence of Zr (and Hf), 1-(2-pyridyl-azo)-2-naphthol (**I**) (at pH 3) is the best indicator Interfering ions, including $Fe^{3+}$, Ni and Cu, are extracted with cupferron (**II**) in diethyl ether from an aq. soln. containing EDTA (pH 1·5). The time taken for a determination is $\simeq 30$ min. *Procedure*— Decompose the sample (200 mesh, 0·5 g) with HC (50 ml) and $NH_4F$ (2 g) and oxidise the Fe with $HNO_3$ (2 ml). Heat with $HClO_4$ (20 ml) until white fumes appear. Dissolve in water (50 ml); fuse the residue, if any, with $Na_2CO_3$, dissolve the melt in HCl (1:4, a few ml), add it to the soln. and make up to 250 ml. Dilute a 25-ml portion together with EDTA (0·0125 $M$, 30 ml) to 100 ml. Adjust the pH to 1·5 with ammonium acetate soln. (50%) add **II** (5%, 10 ml) and extract with ether (80 ml for 1 min. Transfer the aq. layer into aceton (20 ml), adjust the pH to 3·0, add **I** (0·1% in meth anol, 1 or 2 drops) and titrate with $CuSO_4$ soln. (0·0125 $M$ in 0·35 $N$ $H_2SO_4$) to a red colour.

K. Saito

. **Gravimetric determination of zirconium in m.** J. H. Hill and M. J. Miles (Titanium Corp. of America, Henderson, Nev.). *Anal.* 1959, **31** (2), 252–254.—Zirconium is pptd. n HCl soln., containing from 0·15 to 0·2 g by mandelic acid. After filtration, the Zr late is dissolved in aq. $NH_3$ soln. and the filtered to remove any Ti associated with the ppt. After re-pptn., the Zr mandelate is to $ZrO_2$ and weighed. Interference is by Hf and Nb, giving high results. No rence is caused by the presence, in the ts usually found in titanium alloys, of Fe, Sn, Cu, Cr, Co, Mg, Mn, Mo and Ni. The d is applicable to the determination of Zr s and residues, provided that $SO_4^{2-}$ are re- when decomposition has been effected by of $KHSO_4$ fusion; Zr and Ti are pptd. as xides by aq. $NH_3$ soln. and $SO_4^{2-}$ are removed filtrate. The ppt. is re-dissolved in HCl and ocedure carried out as for alloys.

F. L. Selfe

3. **Determination of hydrogen in zirconium e.** W. H. Jones (Wright Air Devel. Center, als Lab., Wright-Patterson AFB, Ohio). *Atomic Energy Comm.*, Rep. WADC-TN-57-957, 9 pp.—The determination is based on easurement of the equilibrium pressure of gen over the metal in a closed system under ermined conditions. The results of analysis amples at temp. ranging from 1900° to 1000° llection times from 10 to 30 min. are reported.

Nucl. Sci. Abstr.

9. **Colorimetric determination of trace amounts alt in zirconium and titanium with the aid of ry cathode electrolysis.** Atsushi Mizuike and Hirano (Inst. Techno-anal. Chem., Fac. of , Tokyo Univ., Hongo). *Japan Analyst*, **7** (9), 545–548.—The electrolytic separation of g of Co, followed by distillation of mercury chmidt and Bricker, *Anal. Abstr.*, 1956, **3**, was examined with $^{60}Co$. By electrolysis for (7·5 V, 1·9 amp.), more than 98% of the Co arated by mercury in *N* $H_2SO_4$ (100 ml) ning $Zr(SO_4)_2$ (≡ 1 g of Zr). Mercury is rated off in a current of N at 350°. Colori- is effected by Sandell's method. *Procedure*— ve the sample (≡ 1 g of Zr) in $H_2SO_4$ (25 ml) ilute to produce 100 ml of *N* $H_2SO_4$ soln. ve titanium metal (1 g) in $H_2SO_4$ (5·1 ml) $I_2O$ and dilute to 100 ml. Electrolyse the vith 2 ml of mercury for 3 hr. with stirring 2 amp.; 0·5 amp. per sq. cm at the cathode). rate off the mercury, dissolve the residue in egia (5 ml) and evaporate to dryness. Add (2·5 ml) and citric acid (0·2 *M*, 1·0 ml), the pH to 7·8 to 8·0 with phosphate buffer ), heat in a water bath with nitroso-R salt ·2%, 0·5 ml), cool in the dark, again heat with (1:1, 2·0 ml) for 4 min., cool and measure tinction at 420 mμ. K. Saito

. **Quantitative spectrographic determination nium in zirconium dioxide.** E. I. Kibisov Inst. Appl. Chem., Leningrad). *Zhur. Anal.* 1958, **13** (6), 653–656.—Two methods, one concn. (0·001 to 0·005%) and the other for concn. (≃3%), have been developed for the determination of Hf in zirconium dioxide. concn. of $HfO_2$, much of the background is eliminated by the use of a discontinuous exposure, and a completely new method of introducing the sample is described. A sample is prepared by mixing 50 mg of ignited and well-ground zirconium oxide for 4 min. in a mortar with 1 ml of glycerol. The hafnium line Hf I 2940·77 was observed at concn. of the order of 0·001 to 0·005%. As a reference line, Zr 2942·3 was used. To determine average concn. of $HfO_2$, spectrographs Q-24 and ISP-22 were used. One drop of the glycerol emulsion of the sample is introduced on to the cold carbon electrode, which is then placed on a hot-plate for 20 min. until all "smoking" ceases. A d.c. arc is used for exciting the spectrum. The gap used is 3·5 mm, the current strength is 6 amp, and the exposure time is 30 sec. As a base line Hf II 2641·4 and as a reference line Zr 2619·2 were used. The glycerol suspensions of the sample should not be stored for more than 12 hr.

W. Roubo

3451. **Determination of small amounts of zirconium and hafnium in silicate rocks.** A. M. Tuzova and A. M. Nemodruk (V.I. Vernadsky Inst. Geochem. and Anal. Chem., Acad. Sci., Moscow). *Zhur. Anal. Khim.*, 1958, **13** (6), 674–676.—A method is described for concentrating Zr and Hf from silicate rocks containing a total of both elements of $0·5 \times 10^{-4}$ to $1 \times 10^{-4}$ %. The procedure involves the pptn. of the elements with phenylarsonic acid followed by re-pptn. by means of *p*-(*p*-dimethylaminophenylazo)benzenearsonic acid (**I**). Take 5 to 10 g of finely divided sample and decompose it in a platinum crucible by means of HCl and HF or $H_2SO_4$ and HF. After decomposition and removal of HF is complete, dissolve the residue in 50 ml of 2 *N* HCl and dilute with water to make the soln. *N* with respect to HCl. Add 1 to 2 ml of 30% $H_2O_2$ soln. (for complexing Ti), then introduce 5 to 6 ml of 20% phenylarsonic acid soln. to precipitate Zr and Hf and allow the ppt. to settle for 24 hr. Filter off and wash the ppt. with a 0·1% soln. of phenylarsonic acid in 0·1 *N* HCl, dry, then ignite for 1·5 to 2 hr. at 900° to 1000°. Fuse the dioxides of Zr and Hf thus obtained with $K_2S_2O_7$, dissolve the melt in 50 ml of 6 *N* HCl and warm on a water bath for 10 to 15 min. After cooling the product, add 1 to 2 ml of 30% $H_2O_2$ soln., 5 ml of a 2% soln. of the sodium salt of **I**, 30 to 35 ml of water and 10 ml of 1% methyl orange soln. After 24 hr. filter off the ppt., wash it 2 or 3 times with a 0·1% soln. of **I** in 0·1 *N* HCl, dry and ignite at 900° to 1000°. Each of the elements is determined in the concentrate thus obtained by X-ray spectral analysis. Since the recovery of the elements is very high (94 to 100%), the accuracy of the method is correspondingly high.

W. Roubo

3452. **Determination of radiogenic helium in zircon by stable isotope dilution technique.** P. E. Damon and J. L. Kulp (Lamont Geol. Observatory, Palisades, N.Y., U.S.A.). *Trans. Amer. Geophys. Union*, 1957, **38**, 945–953.—Zircon samples have been analysed for He by an isotopic dilution technique in which $^3He$ was used as a spike. The precision of this method is about ±3% and gives a He content 15% higher than that given by techniques used by previous investigators. Non-metamict zircon samples studied indicate that a retentivity of He of >80% is not unusual. Metamict zircons retained only 1% of radiogenic He.

Chem. Abstr.

3453. **Analytical chemistry of hafnium.** L. M. Komissarova and V. E. Plyushchev (M.V. Lomonosov State Univ., Moscow). *Zhur. Anal. Khim.*, 1958, **13** (6), 709–715.—A review, with 67 references.
W. Roubo

3454. **Ultra-violet spectrophotometric determination of thorium with 2 : 4-dichlorophenoxyacetic acid.** Sachindra Kumar Datta (Chem. Dept., Darjeeling Gov. Coll., India). *Anal. Chem.*, 1959, **31** (2), 195–197.—*Procedure*—Dilute the soln. (containing 2 to 20 mg of Th as nitrate) to 20 ml and adjust the pH to 2·4. Heat to 80° and precipitate Th by the addition of an excess of a hot 1% soln. of 2:4-dichlorophenoxyacetic acid. Set aside for 5 min. and filter through a No. 3 porosity glass filter-crucible. Wash successively with a 0·1% soln. of the reagent, hot ethanol and diethyl ether. Dissolve the ppt. in 0·08 *M* ammonium carbonate soln. (50 ml), and dilute to 1 litre. Measure the extinction at 230 m$\mu$ against a reference soln. containing the same concn. of ammonium carbonate. Bi- and ter-valent Fe, $Ce^{4+}$ and $Zr^{4+}$ interfere seriously, but only slight interference is caused by Ni, Co and U. Optimum results are obtained with 2 to 14 mg of Th. The accuracy is poor in samples containing $<2$ mg of Th.
F. L. Selfe

3455. **Amperometric titration of thorium in monazite.** Shao-Chun Tung and Er-Kang Wang (Inst. of Appl. Chem., Acad. Sinica). *Acta Chim. Sinica*, 1959, **25** (1), 33–37.—The dried sample (3 g) is fused with $KHF_2$ (12 g) in a platinum crucible. The melt is treated with hot water (70 ml) and HF (20 ml). By employing a mixture of $AlCl_3$ (30 g), acetic acid (17·5 ml) and Na acetate (2 g) in 250 ml as supporting electrolyte, Th is determined by amperometric titration at 25° with standard ammonium molybdate soln. at an applied potential of $-0{\cdot}75$ V *vs.* the S.C.E. The error of the method is $<\pm 2\%$. A complete analysis takes 3 hr.
S. H. Yuen

3456. **Spectrographic determination of scandium, yttrium and the rare earths in thorium.** J. P. Faris (Argonne Nat. Lab., Lemont, Ill., U.S.A.). *Appl. Spectroscopy*, 1958, **12** (6), 157–161.—The thorium is dissolved in 8 *N* $HNO_3$ and passed through a column of Dowex-1 anion resin. The impurities in the eluate are then determined by the copper-spark technique with an accuracy of about $\pm 40\%$ when the spectra are visually compared with standard spectra and of about $\pm 5\%$ when a densitometric procedure is used to evaluate the spectra.
K. A. Proctor

3457. **Conductimetric method for the estimation of small quantities of ammonia.** J. Shaw and B. W. Staddon (King's Coll., Newcastle upon Tyne, England). *J. Exp. Biol.*, 1958, **35** (1), 85–95.—Ammonia is liberated from the sample by alkali (3 to 5 $\mu$l of half-satd. $KBO_2$ soln.) and absorbed in a small drop of standard acid soln. (1 to 3 $\mu$l of $H_2SO_4$, *e.g.*, 0·001 *N*) by Conway's diffusion method. At the end of the diffusion period the acid drop is transferred to a small conductivity cell maintained at constant temp., and made up to the mark with $H_2O$. The conductance of the soln. is measured and the percentage of the acid neutralised is calculated by reference to a calibration curve. The electrical conductance of the acid falls as $NH_3$ is absorbed, owing to the difference in the mobility of $H^+$ and $NH_4^+$. Results for standard $(NH_4)_2SO_4$ soln. and biological fluids are tabulated. The method can be applied to amounts down to 0·005 of ammonia-N with a standard deviation of $<\pm 2$ with 0·001 $\mu$g of ammonia-N the error is $\pm 8$ The construction of small diffusion chambers a small conductivity cells is described.
K. R. C

3458. **Analysis for industry.** A. M. G. Macdon *Ind. Chemist*, 1959, **35** (1), 88–91.—A review given of the use of organic base molybdophospha in the determination of phosphorus.
O. M. Whitto

3459. **Critical factors in the turbidimetric mi determination of phosphorus as strychnine molyb phosphate.** A. J. Hegedüs and M. Dvors (Forschungsinst. f. d. nachrichtentech. Ind., Tu ram, Budapest). *Mikrochim. Acta*, 1959, (1), 1 159.—The determination of traces of P as stry nine molybdophosphate has been studied to as tain the effect of the several variables on the de mination. The following procedure illustra optimum conditions. Transfer the soln. ($>25$ of P) to a 25-ml flask, add 3·7 ml of 8 *N* H and 2·5 ml of strychnine - molybdic acid s (0·2 *M* in $MoO_3$, 4 *M* in $HNO_3$, 0·173 *M* in Na and 0·004 *M* in strychnine nitrate). Dilute soln. to 25 ml, mix and set aside for 1 hr. at before recording the extinction at 720 m$\mu$. Res (20) at a level of 12 $\mu$g of P were all within $\pm 0{\cdot}3$ of P.
T. R. Andrew

3460. **Determination of phosphorus in low-gr uranium ores.** E. Booth [U.K.A.E.A. (Res. Grou Woolwich Outstation, C37, Royal Aresenal, W wich, London]. AERE-AM 7, 1959, 3 pp.—T ore, after sintering at 450° with $Na_2O_2$, is dissol in dil. $HNO_3$ and the P is determined absorp metrically in a suitable aliquot as the molyb vanadophosphate complex. The method is app able to ores containing up to 0·5% of P and coeff. of variation at the 100 p.p.m. level is $\simeq \pm 2$ (*Cf.* Elwell and Wilson, *Analyst*, 1956, **81**, 136.
N. E

3461. **Use of radioactive phosphorus in the st of phosphate separations.** P. H. Bailey and R. W Broadbank (Sch. of Chem., Coll. of Technol. a Commerce, Leicester, England). *Analyst*, 19 **83**, 675–679.—Phosphate ions labelled with have been used to study the efficiencies of the ba acetate, the metallic tin and the zirconium nitr procedures for the removal of $PO_4^{3-}$ in semi-mi qual. analysis. The $^{32}P$ (0·05 to 0·1 $\mu$C) was ad to standard soln. of calcium phosphate or $KH_2P$ In each method the activity of the ppt. and of supernatant liquid was determined, with the nec sary corrections for background activity and l counts, and the percentage of $PO_4^{3-}$ recovered fr the soln. was calculated. Small amounts of PO are efficiently removed from soln. by both the ba acetate and the metallic tin procedures. T procedure with $Zr(NO_3)_4$ is satisfactory provi that an excess of reagent is avoided, especially w small amounts (*e.g.*, 3 to 5 mg) of $PO_4^{3-}$, the o mum ratio being three Zr atoms to two $PO_4^{3-}$ io
A. O. Jone

3462. **Method for determination of oxygen content of inorganic phosphate.** F. R. Williams L. P. Hager (Converse Mem. Lab., Harvard Un Cambridge, Mass., U.S.A.). *Science*, 1958, 1 1434.—In the method described, the phosphat heated in an evacuated tube with $Hg(CN)_2$ at 2

hr. The $CO_2$ formed is collected and intro- d into the mass spectrometer for measurement ). H. F. W. KIRKPATRICK

63. **Analysis of commercial sodium tripoly- phate by reverse-flow ion-exchange chromato- ıy.** R. H. Kolloff (Monsanto Chemical Co., Louis, Mo., U.S.A.). *Bull. A.S.T.M.*, 1959, , 74–80.—Apparatus and procedure are de- ed whereby a complete and accurate analysis mmercial $Na_5P_3O_{10}$ can be made in $<90$ min. ln. of the sample ($\simeq 20$ mg), together with aq. Cl (pH 5), is passed through a column (37 cm cm) of Dowex 1X-10 (200 to 400 mesh, Cl ) by the pressurised continuous-gradient ow" elution technique (Grande and Beuken- , *Anal. Chem.*, 1956, **28**, 1497; Schwab *et al.*, , 1957, **29**, 1357). The total pressure applied e column is $\simeq 200$ cm of water for a flow-rate of nl per min. The order of elution of the ions is—ortho-, pyro-, tri-, tetrameta- and eta-phosphate; long-chain phosphates are re- d on the column and can be determined by rence. A quant. determination of the phos- e in each fraction (one only for each com- ıd) is made by an improved and standardised rophotometric procedure based on the molyb- m blue method. The reverse-flow elution and iner resin particles ensure a sharper separation he phosphate species. The method is more rate and rapid than the ion-exchange procedure ı previously (*cf.* Spangler *et al.*, *Anal. Abstr.*, , **6**, 516). W. J. BAKER

64. **Colorimetric determination of arsenic in - arsenic alloys.** Takashi Miura and Masao i (Matsushita Electric Ind., Chigasaki, Kana- a-ken). *Japan Analyst*, 1958, **7** (11), 718–720.— erimental conditions for the rapid (3 hr.) rimetric determination of As in lead alloy taining 2 to 10% of As) were examined. The ybdenum blue method is useful for $<0{\cdot}6$ mg s per 100 ml; the influence of segregation in the is eliminated by taking a large amount of ple. *Procedure*—Dissolve the sample (4 g) in $O_3$ (1:3, 30 ml) and $H_2O_2$ (30%, 10 ml), then with $H_2SO_4$ (1:1, 10 ml), cool, and make o 1 litre (without filtration). Make a 10-ml ıot alkaline with 3 *N* NaOH, boil to expel $_2$, make acid with $H_2SO_4$ (1:10) and dilute to ml. Acidify a 50-ml aliquot with $HNO_3$ , 2 ml), neutralise with 3 *N* NaOH and make o 100 ml after addition of $H_2SO_4$ (1:10, 10 ml), $_4)_2MoO_4$ soln. (2%, 4 ml) and hydrazine sulphate (1%, 15 ml). Immerse in boiling water for in., cool, and measure the extinction at 750 mμ. K. SAITO

65. **Precise micro-heterometric determination smuth as iodide with Pyramidon [amidopyrine]. tudy of the reaction and of the compounds.** Bobtelsky and M. M. Cohen (Hebrew Univ., salem). *Anal. Chim. Acta*, 1959, **20** (1), 1–15.— metric methods are described for the deter- tion of Bi and amidopyrine (**I**) by the hetero- ic titration procedure (Bobtelsky, *Anal. . Acta*, 1955, **13**, 172). Bismuth ($\simeq 1$ mg) in *M* $HNO_3$ containing KI is titrated with 25 *M* **I**. In the reverse procedure, **I** is titrated 0·005 *M* $Bi(NO_3)_3$. The method is rapid and rate and is unaffected by the presence of line-earth and heavy metals up to 80 to 90% e total metal content. W. T. CARTER

3466. **Complexometric titrations (chelatometry). XLI. Photometric titrations of bismuth and copper using catechol violet as indicator.** V. Suk and V. Miketuková (Inst. Anal. Chem., Charles' Univ., Prague). *Chem. Listy*, 1958, **52** (12), 2408–2409.— *Procedure for Bi*—Dilute the soln. of $Bi(NO_3)_3$ in the photometric titration cell to 70 to 100 ml, add catechol violet soln. (**I**) (0·1%) (3 to 4 drops) as indicator, adjust the pH to 2 to 3 with aq. $NH_3$ till blue, and titrate photometrically with 0·01 *M* EDTA (disodium salt) (**II**) till yellow, with the use of a yellow filter; 0·2 to 140 mg of Bi can be determined with an accuracy of $\pm 0{\cdot}11\%$. Interference by $Fe^{3+}$ can be avoided by the addition of ascorbic acid. *Procedure for Cu*—Dilute the soln. of $Cu^{2+}$ to 70 to 100 ml with water, add $NH_4NO_3$ soln. (10%) (5 ml), 4 to 5 drops of **I** and aq. $NH_3$ dropwise till blue. Add Na acetate soln. (20%) (5 ml) and titrate with **II** till green, with the use of a yellow filter; 1 to 35 mg of Cu can be determined with an accuracy within $\pm 0{\cdot}08\%$. The titrations were carried out with the use of a Lange photometer and the end-point was determined graphically. J. ZÝKA

3467. **Effect of pre-saturation of the paper on the sequence of bismuth - cadmium in paper chromatography with butanol - normal hydrochloric acid.** J. A. Coch-Frugoni (Lab. Curie, Inst. du Radium, Paris). *J. Chromatography*, 1959, **2** (1), 69–71.— When a mixture containing Bi and Cd is chromatographed with this solvent system without previous saturation of the paper, Cd precedes Bi, but when the paper is brought into equilibrium by exposure to the solvent vapour for 24 hr. the order is reversed. Pre-saturation does not improve the separation, but the effect is important in the measurement of $R_F$ values. G. BURGER

3468. **Spectrophotometric determination of vanadium by extraction of tungstovanadophosphoric acid with ethyl methyl ketone.** Hiroshi Kitagawa and Norio Shibata (Hitachi Central Res. Lab., Kokubunji, Tokyo). *Japan Analyst*, 1958, **7** (10), 624–627.—Tungstovanadophosphoric acid is extracted from 0·5 *N* $H_2SO_4$ soln. with ethyl methyl ketone (**I**). The extinction at 440 mμ is proportional to the concn. of V for $<0{\cdot}8$ mg per 25 ml of **I**. There is no interference from coloured ions, including $Fe^{3+}$ ($<5$ mg), Ni, Co, Mn and Cu ($<200$ mg each). Chromium is removed as chromyl chloride. *Procedure*—Heat the sample soln. to white fumes with $H_2SO_4$ (1:1, 3 ml), dissolve in HCl (1:1, 10 ml) and water (20 ml), neutralise with NaOH soln. (6 *N*) and make up to 50 ml after the addition of $H_2SO_4$ (5 *N*, 5 ml) and $H_3PO_4$ (1:2, 1 ml). Heat the product to 100°, add $Na_2WO_4$ soln. (0·5 *M*, 0·5 ml), then cool and extract with **I** saturated with 0·5 *N* $H_2SO_4$. K. SAITO

3469. **Determination of vanadium and chromium by photometric titration.** V. F. Barkovskiĭ (Ural State Inst. A.M. Gorky, USSR). *Zhur. Anal. Khim.*, 1958, **13** (6), 682–685.—*Determination of V in ferrovanadium*—Dissolve the ferrovanadium (0·05 g) by heating in $H_2SO_4$ (1:3) (5 ml), add $HNO_3$ (1:1) (1 ml) and heat for 1 to 2 min., cool, make up to 60 to 70 ml with $H_2O$, add $KMnO_4$ soln. dropwise until a stable pink colour is obtained; decompose the excess of $KMnO_4$ with satd. oxalic acid soln. and titrate photometrically with 0·02 ***N*** $(NH_4)_2SO_4.FeSO_4$. *Determination of V in steel containing no W*—To the sample (1 to 3 g) add $H_2O$ (30 ml) and 25 ml of an acid mixture (15 ml of

$H_2SO_4$, sp. gr. 1·84, and 10 ml of $H_3PO_4$, sp. gr. 1·7); dissolve by heating, decomposing the carbides by the addition of conc. $HNO_3$ (0·5 ml), and continue as described above. *Determination of V in steel as a phosphorus - tungsten - vanadium complex*—Dissolve the steel (0·2 to 1·0 g) by heating with 15 to 20 ml of an acid mixture ($H_2O$, $H_2SO_4$, sp. gr. 1·84, and $H_3PO_4$, sp. gr. 1·7) (1:1:1), decompose the carbides with $HNO_3$, cool, make up to 60 to 70 ml with $H_2O$, and if W is absent from the steel add 0·05 *N* sodium tungstate (5 ml); add $KMnO_4$ soln. and continue as described above. *Determination of V and Cr in a single steel sample*—Dissolve the sample (0·5 g) by heating in 30 ml of an acid mixture (380 ml of $H_2O$, 90 ml of $H_2SO_4$, sp. gr. 1·84, and 60 ml of $H_3PO_4$, sp. gr. 1·7), decompose the carbides by the dropwise addition of $HNO_3$, evaporate the soln. until $H_2SO_4$ fumes appear, add hot $H_2O$, and if W is absent from the steel add 0·05 *N* sodium tungstate; add 0·5% $CoSO_4.7H_2O$ soln. (10 ml) and heat to boiling; add freshly prepared 25% $(NH_4)_2S_2O_8$ soln. (20 ml) to the boiling soln. and continue boiling for a further 1 to 2 min. until a crimson permanganate colour appears. Place the soln. on a hot-plate until the $(NH_4)_2S_2O_8$ is completely decomposed and then boil again; add 5% NaCl soln. (10 ml) and continue heating for 5 to 10 min. after the permanganate colour is discharged. Titrate the cool soln. with 0·05 *N* $(NH_4)_2SO_4.FeSO_4$. The absolute error did not exceed 0·05% and the relative error was between +0·01 and −0·09%, according to the sample used.

K. R. C.

3470. **Separation of vanadium, molybdenum and tungsten by paper chromatography. I.** Shih-fu Tzou and Shu-chuan Liang. *Acta Chim. Sinica*, 1958, **24** (5), 383–387.—The method of Pollard has the disadvantages that (*i*) tailing takes place with V and Mo and (*ii*) W remains at the origin, which tends to retain some Mo. By keeping the valency and the state of association unchanged during elution and by forming stable and soluble complexes of the elements to be tested, these faults can be avoided. The per-acids formed by V, Mo and W with $H_2O_2$ were found to be satisfactory. Seven eluents were tested, Nos. 1, 2 and 3 comprising *n*-butanol - $H_2O_2$ - $HNO_3$ in slightly different ratios; the $R_F$ values are almost the same. Eluents 4 and 5 comprise the first three solvents containing dioxan and benzoylacetone, respectively. The $R_F$ values for V, Mo and W with eluents 4 and 5 are several times as great as those with eluents 1 and 2. In eluents 6 and 7, $(NH_4)_2S_2O_8$ is used instead of $H_2O_2$; the results are not promising as the spots of V and W diffuse to a pronounced degree and the spot of W moves very little ($R_F = 0·01$). A table of $R_F$ values is given for the three elements when chromatographed singly and in admixture, and diagrams of typical chromatograms are given. The separation of $V^V$, $Mo^{VI}$ and $W^{VI}$ from one another is possible with eluents 1 to 3. With eluents 4 and 5 it is possible to separate V from Mo, Mo from W, and Mo from both V and W, but it is impossible to separate V and W. With eluents 6 and 7 it is possible only to separate Mo from V and V from Mo.

Sci. Abstr. China

3471. **Total assay of high-purity niobium metal by differential spectrophotometry.** R. O. Backer, V. R. Wiederkehr and G. W. Goward (Westinghouse Electric Corp., Bettis Plant, Pittsburgh). *U.S. Atomic Energy Comm.*, Rep. WAPD-204, 1958, 10 pp.—Samples are dissolved in HF and $HNO_3$ and fumed with $H_2SO_4$. Niobium is determi by differential spectrometric measurement of peroxyniobate complex formed in a mixture $H_3PO_4$ and $H_2SO_4$. The method covers a con range of from 92·3 to 100·0% of niobium. relative standard deviation of the method approx. ±0·1%.

Nucl. Sci. Abstr

3472. **Colorimetric determination of tantalum presence of niobium.** G. Popa, D. Negoiu and Baiulescu (Fac. of Chem., "C. I. Parhon" Un Bucharest, Romania). *Z. anal. Chem.*, 1959, (1), 16–19.—The colour reactions of Ta and with three flavone derivatives are examined; forms coloured complexes with quercetin (**I**) with 3-hydroxy-5:7:3′:4′-tetramethoxyflavone, not with 5-hydroxy-3:7:3′:4′-tetramethoxyflavo Nb reacts with none of the three reagents. T Ta can be determined in the presence of Nb. Ta soln. (prepared from $Ta_2O_5$ by fusion w $KHSO_4$ and dissolution of the melt in 3% amm ium oxalate) is treated with a soln. of **I** [0·1% ethanol - conc. HCl (3:1)] (5 ml) and diluted 10 ml with ethanol; the extinction is then measu in a Pulfrich photometer (1-cm cell) with a M filter; 5 to 80 μg of Ta in 10 ml can be determi in the presence of a fivefold excess of Nb.

J. P. Stern

3473. **Extraction of sulphur-35 from pile-irradia potassium chloride.** R. G. Deshpande (Ato Energy Estab., Trombay, Bombay, India). *Chromatography*, 1959, **2** (1), 117–118.—Carri free $^{35}S$ produced by irradiation of KCl can separated from $K^+$ and $^{32}P$ by means of a colum Amberlite IRA-400 resin in the $Cl^-$ form. aq. soln. is passed down the column which is t washed with water. The percolate and wa contain some $^{32}P$. The column is then eluted w 0·1 *M* HCl and the eluate collected in 50-ml fr tions. The first few fractions contain $^{32}P$ free fr $^{35}S$, and the later fractions contain pure $^{35}S$, giv complete separation.

G. Burgei

3474. **Collection and turbidimetric estimation sulphur trioxide in flue gases.** D. H. Napier a M. H. Stone (Brit. Coal Utilisation Res. A Leatherhead, Surrey). *J. Appl. Chem.*, 1958, (12), 787–793.—The improved turbidimetric p cedure described enables $SO_3$ in the concn. ra 6 to 80 mg per litre to be determined with a p cision of ±2% and with a lower precision in range 1 to 6 mg per litre. The improveme include temp. control during pptn., the addition solid $BaCl_2$ of standard purity, and the control the aq. *iso*propyl alcohol soln., the concn. of wh is kept at 39·5% by wt. An improved sampl apparatus is also described, together with modifi tions to a commercially available turbidimeter.

J. H. Waton

3475. **Paper-chromatographic separation several inorganic anions containing sulphur and th identification by infra-red spectrography.** Y. Garn and C. Duval (École Nat. du Chim., Paris). *Chromatography*, 1959, **2** (1), 72–75 (in French) The chromatographic behaviour of $SO_4^{2-}$, $HSO_3^-$, $S_2O_7^{2-}$, $S_2O_6^{2-}$, $S_4O_6^{2-}$ and $S_5O_6^{2-}$ has been stud with the solvent systems *n*-butanol - $H_2O$ and *i* propyl alcohol - $H_2O$. The chromatograms w developed with ethanolic benzidine and KMn the bands cut out and the anions dissolved in H for spectrographic determination. The method suitable for the determination of microgram quan ties; $R_F$ values are recorded.

G. Burgei

3476. **Colour reaction for sulphate ion.** H. Weisz st. f. anorg. u. allg. Chem., Tech. Hochsch., enna). *Mikrochim. Acta*, 1959, (1), 26–28.—lphate ion (0·5 $\mu$g) can be detected by spotting e test soln., weakly acid with acetic acid, on a per that has been treated successively with drops 0·1% $Ba(NO_3)_2$ soln., 1% Na rhodizonate soln. d 0·5% $AgNO_3$ soln. The intense violet colour Ag rhodizonate makes the test more sensitive an the simple liberation of rhodizonic acid. terference by halides and sulphides is overcome adding excess of $AgNO_3$ to the test drop. Chro-ate and phosphate do not interfere.

T. R. Andrew

3477. **Analysis of mixtures of sulphuric acid with ner acids by non-aqueous titration.** Mihir Nath as and Debabrata Mukherjee (Jadavpur Univ., lcutta, India). *Anal. Chem.*, 1959, **31** (2), 233–7.—Procedures are given, and discussed, for the tentiometric titration of $H_2SO_4$ as a mono- or basic acid with 0·1 *N* NaOH in ethanediol or in anediol - acetone (2:1). Provided that weak ids are absent, 0·1 *N* piperidine is preferred to aOH as titrant in glycolic media. The method is plicable quant. to binary mixtures of $H_2SO_4$ th $HNO_3$, HCl, $HClO_4$, $H_3PO_4$, acetic acid, sali-lic acid or toluene-*p*-sulphonic acid and also, t with much less accuracy, to ternary mixtures ntaining, in addition to $H_2SO_4$, a weak acid and a rong or moderately strong acid (*e.g.*, a mixture of $SO_4$, $H_3PO_4$ and salicylic acid). When $H_3PO_4$ is esent, the titration is preferably made with NaOH piperidine in ethanediol - *iso*propyl alcohol (2:1). ie conductimetric titration of $H_2SO_4$ with piperi-ne in glycolic media also gives two inflections in e titration curve.

W. J. Baker

3478. **Analysis of sulphonyl chlorides by "polaro-ltric" titration with sodium sulphide.** M. R. F. shworth, W. Walisch and G. Kronz-Dienhart nst. for Org. Chem., Univ. of the Saar, arbrücken, Germany). *Anal. Chim. Acta*, 1959, (1), 96–98.—Sulphonyl chlorides in 50% aq. etone can be titrated with standard $Na_2S$ soln. the range 0·05 to 0·1 *M* a colour change indicates e end-point, but if a "polarovoltric" apparatus is ed with polarised platinum electrodes, potentio-etric titrations can be carried out with soln. as lute as 0·005 *M*.

W. T. Carter

3479. **Application of thio salts in analysis. II. timations based on the decomposition of thio salts. rt F. Estimation of selenium and tellurium in enites and tellurites.** G. B. S. Salaria (Chem. ept., Gov. Coll., Rohtak, Punjab, India). *Anal. im. Acta*, 1958, **19** (6), 604–605.—Quadrivalent e and $Se^{IV}$ may be pptd. as sulphides in readily llected form by addition of $Na_2S$ soln. (2 *N*) and bsequent acidification of the soln. with HCl to N followed by heating almost to boiling-point.

T. R. Andrew

3480. **Micro-determination of chromium in colla-n sutures.** E. R. Hoffmann and M. G. Comfort thicon Inc., Somerville, N.J., U.S.A.). *Micro-em. J.*, 1958, **2** (2), 263–275.—The sutures (3 to mg of dried material) are mineralised by fusion th potassium peroxydisulphate (400 to 800 mg) a platinum or quartz crucible. After dissolution the melt, the Cr is oxidised to the sexavalent te with hypobromite. Excess of oxidant is moved and the Cr is caused to react with a large cess of *sym.*-diphenylcarbazide soln. at pH 1·1, and the extinction is measured at 542 m$\mu$. The standard deviation on 3 to 12-mg samples containing 0·4 to 0·8% of $Cr_2O_3$ is $\pm$0·006. A single determination, including weighing of sample, is completed in $<$15 min.

D. F. Phillips

3481. **Rapid determination of the chromate ion by means of a detector tube.** Yoshitaka Kobayashi (Fac. of Engng, Yokohama Univ., Minami-ku). *Japan Analyst*, 1958, **7** (9), 560–564.—Silica gel (60 to 80 mesh) is impregnated with Pb acetate (0·4 mg per 1 g of the gel) and placed in a glass tube (diam. 2 mm, length of the silica gel column, 60 to 80 mm). When the column is percolated with the sample soln. ($>$2 p.p.m. of $CrO_4^{2-}$), a yellow layer is produced, the length depending on the concn. of the $CrO_4^{2-}$. The influence of grain size, water content of the gel and diameter was examined. The length of the coloured layer is independent of the pH in the range 2·0 to 8·0 and of the temp. (15° to 60°). The coloration is complete within 3 min. and remains unchanged for $>$10 min. The error is $<$10%.

K. Saito

3482. **Iron analysis in chromium solutions.** A. Salka. *Metal Finish.*, 1958, **56** (12), 64.—The upper limit of Fe permissible in the chromium-plating bath is $\simeq$15 to 20 g per litre. Iron is separated as $FePO_4$ and determined by complexo-metric titration with EDTA and ferron as indi-cator. The EDTA - Fe complex (**I**) shows a greater stability than the ferron - Fe one and, when all Fe has been changed into **I**, the end-point is marked by a sudden change in colour from green to yellow. The reagent is specific, but $Cr^{3+}$ interfere and should be oxidised by $(NH_4)_2S_2O_8$.

S.C.I. Abstr.

3483. **Determination of small quantities of molyb-denum in tungstates.** C. Winterstein. *Z. Erzbergb. Metallhüttenw.*, 1957, **10**, 549–551.—Dilute the alkaline soln., obtained by fusion of the specimen and extraction with water, to a known vol. ($MoO_3$ content $>$0·01 g per ml). Treat the soln. (50 ml) with 30 ml of NaF soln. (20 g of NaF, 400 to 450 ml of $H_2O$ and a few ml of 20% NaOH soln., heat, filter and dilute to 500 ml) and neutralise with $H_2SO_4$ (1:1), then add $H_2SO_4$ (1:1) (10 ml) in excess and stir to liberate $CO_2$. Cool to 12° to 15° and place in a separating-funnel. Add 10% KSCN soln. (10 ml), 3 ml of $SnCl_2$ soln. [10 g of $SnCl_2.2H_2O$ is dissolved in 30 ml of HCl (sp. gr. = 1·19) and diluted to 100 ml] and finally 85% butyl acetate (20 ml). Shake for 30 to 40 sec. and pass the lower layer into the original beaker. Repeat the shaking in the separating-funnel twice. The extraction is complete when the butyl acetate layer is colourless. Finally dilute the extract to 50 ml with butyl acetate and measure the colour with a Hg 436 filter. The extinction max. is at 470 m$\mu$.

Chem. Abstr.

3484. **The use of metal-specific indicators in precipitation titrations. III. Determination of tungsten and molybdenum in synthetic samples.** E. Lassner, R. Scharf and R. Püschel (Metallwerk Plansee A.-G., Reutte/Tirol, Austria). *Z. anal. Chem.*, 1959, **165** (1), 29–32.—The method previously described (*cf.* Püschel *et al.*, *Anal. Abstr.*, 1959, **6**, 1719, 2126) is suitable for the rapid (30 min.) routine determination of W as tungstate in metal samples containing Cu, Ni, Fe and Th and in mixed carbides of W, Ti and Ta, and of Mo as molybdate in molybdenum concentrates. In

samples containing both W and Mo, simple titration gives the sum of the metals; in an aliquot, Mo is then separated by $H_2S$ (W being masked by tartrate) and gravimetrically determined. For tungsten samples containing 80 to 98% of W, the average error is ±0·25%, and for molybdenum concentrates (60% of Mo) it is ±0·3%. Results agree with gravimetric results. *Procedure*—(*a*) Dissolve the tungsten sample (10 g) in HF - $HNO_3$, evaporate to dryness, and fuse the residue with $NaKCO_3$. Dissolve the melt in water, dilute to 1 litre, filter, and use 10 ml. (*b*) Fuse the molybdenum sample (2·5 g) with $Na_2O_2$ and dissolve the melt in water; add $Na_2O_2$ (1 g) and boil. Dilute the cold soln. to 1 litre, filter, and use 10 ml. Dilute the 10-ml aliquot from (*a*) or (*b*) to 250 ml, adjust to pH 2 to 3 with dil. $HNO_3$, and boil for some minutes. Add hexamine (1 g) and 0·1% aq. 4-(2-pyridylazo)resorcinol soln. (8 to 10 drops), as indicator, and titrate the boiling soln. with 0·1 *M* $Pb(NO_3)_2$ (added dropwise with stirring) to a persistent red colour. J. P. Stern

3485. **Determination of uranium by cupferron with Complexone III as the masking agent.** A. K. Majumdar and J. B. Ray Chowdhury (Jadavpur Univ., Calcutta, India). *Anal. Chim. Acta*, 1958, **19** (6), 576–577.—By pptn. with cupferron at pH 6 to 7 in a soln. containing a ten-fold excess of EDTA (disodium salt), U can be separated from Bi, Cu, Fe, Cr, Al, Th, Cd, Pb, Zn, Mn, Ni, Co, rare-earth metals, $VO_3^-$, $MoO_4^{2-}$ and $WO_4^{2-}$; Ti, Be, Sn, Sb, As and $PO_4^{3-}$ interfere. T. R. Andrew

3486. **An extraction, controlled-potential coulometric method specific for uranium(VI).** G. L. Booman and W. B. Holbrook (Atomic Energy Div., Phillips Petroleum Co., Idaho Falls, U.S.A.). *Anal. Chem.*, 1959, **31** (1), 10–16.—*Cf. Anal. Abstr.*, 1959, **7**, 905.

3487. **New method based on paper chromatography for the determination of uranium in uranium minerals.** I. I. M. Elbeih and M. A. Abou-Elnaga (Dept. of Chem., Univ. of Cairo, Giza, Egypt). *Chemist Analyst*, 1958, **47** (4), 92–93.—The mineral (0·5 g for rich ores, up to 5 or 10 g for poor ones) is dissolved in a mixture of 10 ml of conc. $HNO_3$ and 1 to 2 ml of conc. HF with the aid of heat, and taken almost to dryness. The $SiO_2$ residue is extracted with 3 ml of conc. $HNO_3$ and 20 ml of hot water, filtered off and dried. The dissolution and extraction steps are repeated, and the united filtrates and washings made up to 100 ml. For rich ores, 0·01-ml spots are chromatographed as previously described for the visual comparison procedure (*Anal. Abstr.*, 1959, **6**, 855), the uranium spots being located on indicator strips with $K_4Fe(CN)_6$, and appropriate portions of the main paper, together with blanks, cut off and transferred to separate flasks. EDTA titration is carried out by the method of Kinnunen and Wennerstrand (*Chemist Analyst*, 1957, **46**, 92). The paper carrying a spot is shredded, treated with glacial acetic acid (1 ml), water (15 ml) and 0·001 *M* EDTA soln. (disodium salt) (5 ml), and boiled gently for 10 min. Ascorbic acid (0·2 g) is added, the mixture boiled gently for 10 min., cooled to 30°, and the excess of EDTA back-titrated with 0·001 *M* $Th(NO_3)_4$ soln., with xylenol orange as indicator. The mean of four such titrations is obtained, and corrected by the mean of four similar titrations carried out on blank spots. For poor ores, ten spots each of 0·01 ml of soln. are chromatographed as before on a wide paper, the appropriate zones of the test and blank paper being cut out and treated as described above. Tervalent Bi, $Th^{3+}$, $Sn^{2+}$ and $Sn^{4+}$ are not separated by the chromatographic procedure, and interfere with the EDTA titration, but not with the visual comparison procedure. Results for known amounts of U from 20 to 100 μg showed errors of from −1·0 to +1·2 μg. Six analyses of an Egyptian phosphate rock, using ten zones for each titration, showed recoveries from 0·009 to 0·011% of U (mean 0·010%), the result by a standard method being 0·01%. R. E. Essery

3488. **Radiometric determination of uranium in ores.** L. G. Evans and C. Rampacek (U.S. Bur. of Mines, Tucson, Arizona). *U.S. Bur. Mines, Rep. Invest.*, 1958, (5390), 15 pp.—Rapid determinations were investigated and the two most promising ones were developed, namely the ratio and equilibrium methods. The ratio method consists in determining the radioactivity of the unknown sample by a Geiger counter and standard scaler counting unit under three different conditions. An open radioactivity count is first made on the material, followed by the determination of the radioactivity through a aluminium filter and then through a lead filter. The open counting procedure records both the weak and the strong β-rays and about 5% of the γ-rays; while the aluminium filter passes only the stronger β-radiations and γ-rays; the lead filter removes substantially all the β-radiations and allows only the γ-rays to pass. By comparing the ratios of the open count to the counts obtained through the aluminium and lead filters it is possible to predict whether or not a sample is in or near radioactive equilibrium and whether the radioactivity is due to the presence of Th. The equilibrium method depends on the simultaneous measurement of the β- and γ-radiations given off by an ore. The apparent equiv. uranium content of the sample is then determined by comparing its β-activity with that of known assayed pitchblende standards in radioactive equilibrium. In a similar way the apparent equiv. uranium content of the sample is determined from the γ-activity. The true uranium content of the ore is then calculated from these two values. The radiometric results obtained from 100 random samples in various stages of equilibrium by the ratio method and by a modified equilibrium method are discussed. The sample contained 0·01 to 3·64% of $U_3O_8$ as determined by chemical analysis. The over-all accuracy of the equilibrium method was 28·1%. By comparison the over-all error between the chemical analyses and the β-equiv. uranium values of the ratio method was about 200%. However, the error was only 16·2% for samples shown to be in equilibrium by the ratio method. The two methods are useful for distinguishing between ores that are in or out of radioactive equilibrium. Neither the ratio method nor the equilibrium procedure is a substitute for quant. chemical analysis, but either is useful as a control for detecting samples not worth chemical analysis. K. R. C.

3489. **Determination of uranium in flotation concentrates and in leach liquors by X-ray fluorescence.** G. L. Smithson, R. C. Eager and A. E. VanCleave (Dept. of Chem., Univ. of Saskatchewan, Saskatoon, Canada). *Canad. J. Chem.*, 1959, **37** (1), 20–28.—Approximate results for U are obtained by direct measurement on flotation concentrates, but more accurate results are obtained by the use of an internal standard, *e.g.*, Sr or Y. This method is

ter than the conventional chemical or fluoric ones. Uranium in the organic phases ained in liquid - liquid extraction studies can letermined. An aq. soln. of the internal standis added to the sample, dispersion is facilitated he addition of abs. ethanol, the sample is dried ground for 30 min. and the significant part of X-ray spectrum is recorded or determined by ing the spectrogoniometer at $2\theta$ angles and nting for 100 sec. The background count at position of the peak is interpolated from the kground count on either side of the peak. nium in organic solvents is determined by the of Br, added as bromobenzene, as the internal ndard. The lower limit of determination of $_8$ is $\simeq 0{\cdot}02\%$ in solids and 0·1 mg per ml in soln. n in flotation concentrates and leach liquors can similarly determined. S.C.I. Abstr.

490. **Determination of $UO_3$ and $U_3O_8$ in brown de.** L. G. Stonhill (Metall. Lab., Eldorado ning and Refining Ltd., Ottawa, Canada). *ad. J. Chem.*, 1958, **36** (11), 1487–1492.—rown oxide", produced by the incomplete reduc- of $UO_3$ with H, is a mixture of $UO_3$, $U_3O_8$ and $_2$. Its content of $UO_3$ can be obtained by the raction (for $\simeq 15$ min.) of 325-mesh material h hot 5% ammonium citrate soln. and deterination of the loss in weight of the sample. The $_3$ and $U_3O_8$ in a fresh sample can be dissolved in % (v/v) $H_3PO_4$ at 100° in an atmosphere of $CO_2$, the total $U^{VI}$ can be titrated potentiometrically the same flask) with dil. $Ti_2(SO_4)_3$ in $H_2SO_4$ at to 85° in the presence of $FeSO_4.(NH_4)_2SO_4$ 0·25 g). The $UO_3$ equiv. to the $U_3O_8$ can then calculated, and hence the content of $U_3O_8$ and, difference, of $UO_2$. The value for total U, culated from the three results, is in good agreent with that given by the gravimetric and colorimetric methods, respectively. W. J. Baker

3491. **Polarographic estimation of soluble silica uranyl nitrate.** A. K. Sundaram and M. Sunresan (Anal. Div., Atomic Energy Estab., Trom, Bombay, India). *Anal. Chim. Acta*, 1958, **19**, 601–603.—Soluble silica is determined by the dition of ammonium molybdate to an acid soln. d polarographic determination of the molybdocate. *Procedure*—To 2·5 ml of $NH_4NO_3$ soln. *N*), 0·5 ml of ammonium molybdate soln. (5%), ml of $HNO_3$ (9·2 *N*) and 0·2 ml of gelatin soln. 05%) in a 10-ml flask add 1 g of sample dissolved 2 ml of $H_2O$ and dilute to 10 ml. Record the arogram from 0 to $-0{\cdot}15$ V *vs.* the mercury ol. A blank is carried out in the basal soln. e from uranyl nitrate. Results are within .0% for 10 to 100 p.p.m. of $SiO_2$; Cu, Fe (>1 .m.) and V (>5 p.p.m.) interfere, but interfere due to Cu can be eliminated by adding 2 ml satd. salicylic acid soln., which also minimises erference from Fe. T. R. Andrew

3492. **Colorimetric determination of fluorine.** A. Guntz and M. Arène (Lab. de Chim. Appl., . des Sciences, Algiers). *Chim. Anal.*, 1958, **40**, 453–457.—The empirical thorium alizarinphonate method previously described (*cf. Anal. str.*, 1958, **5**, 3729) has been studied with respect the effect of pH, of the concn. of reagents and of influence of $Cl^-$ and $SO_4^{2-}$, results being pretted as graphs. Working at pH 2·9 (0·02 *M* broacetic acid, semi-neutralised) and a constant cn. of Na alizarinsulphonate (51·3 mg per litre), Th - F ratio is $<1$ for low extinctions and $>1$ for high ones, and a nomogram is given for the calculation of F, related to Th and extinction. Sulphate interferes by competing with F for the Th in the lake, but the total decrease in extinction is smaller than the sum of those due to the two ions separately. A nomogram is given from which, given the $SO_4^{2-}$ (determined turbidimetrically) and the extinction, the F can be obtained. Under the given conditions, $Cl^-$ do not interefere if the concn. is $<10$ g per litre. Fluorine in six Algerian waters ranges from 0·08 to 1·10 mg per litre. R. E. Essery

3493. **Rapid complexometric titration of fluoride ion.** S. Wilska (Dept. of Chem., Inst. of Technol., Helsinki, Finland). *Suomen Kem., B*, 1958, **31** (12), 400–401.—The usual complexometric method, which is based on pptn. of $CaF_2$ and back-titration of the excess of $Ca^{2+}$ with EDTA, is modified so that the determination can be performed in 5 min. E. Sjöström

3494. **Determination of fluoride by conductimetric titration.** H. Kubota and J. G. Surak (Anal. Chem. Div., Oak Ridge Nat. Lab., Tenn., U.S.A.). *Anal. Chem.*, 1959, **31** (2), 283–286.—The reaction between fluoride and lanthanum ions is used in this semimicro determination in which the end-point is located by changes in the conductivity of the reaction medium. Milligram quantities of fluoride in solution can be determined with good accuracy and precision, if the total amount of extraneous ions is small. A modified semi-micro distillation apparatus is employed to carry out a distillation at constant temp. and vol., and this distillation minimises the amount of extraneous ions present in the titration medium. K. A. Proctor

3495. **Chlorine in distilled water as a source of laboratory error.** W. T. Caraway (McLaren Gen. Hosp., Flint, Mich., U.S.A.). *Clin. Chem.*, 1958, **4** (6), 513–518.—Distillation of chlorinated tap water may result in significant contamination of the distillate with free chlorine. The detection of free Cl and its effect on a number of the usual clinical laboratory determinations are discussed. H. F. W. Kirkpatrick

3496. **Use of methyl chloride for the mass-spectrometric analysis of chlorine isotopes.** W. Herzog and E. Dörnenburg (Max Planck Inst. Chem., Mainz, Germany). *Z. Naturf.*, 1958, **13a**, 51–52.—Methyl chloride is especially suited for the analysis of chlorine isotopes with the mass spectrometer because this compound does not show any memory effects. After conversion of the Cl to be analysed into AgCl, the AgCl was reduced at 600° in a stream of hydrogen and the HCl formed was absorbed in aq. $NH_3$. By evaporation of the soln., the $NH_4Cl$ used as starting material for an analysis was obtained. By treating 50 mg of $NH_4Cl$ with 5 ml of a mixture of $H_2SO_4$ (240 ml), $H_2O$ (40 ml) and methanol (350 ml) a small amount of methyl chloride is formed, which is transferred to the mass spectrometer. The amount of gas formed from 10 mg of $NH_4Cl$ during 10 min. at 80° is sufficient to determine the isotope distribution in chlorine to within 0·5%. Chem. Abstr.

3497. **A spot test for chloride.** E. Phillips (Douglas Aircraft Co. Inc., El Segundo, Calif., U.S.A.). *Chemist Analyst*, 1958, **47** (4), 102.—For the detection of $Cl^-$ or $Br^-$ on corroded metal surfaces, immerse filter-paper in 0·25 *M* $AgNO_3$ in 0·1 *M* $HNO_3$. Apply the wet paper to the sample

surface, cover with a polyethylene film, and press on the surface for 5 min. Remove the paper and expose it to ultra-violet radiation or strong sunlight. A red, purple or grey discoloration on the paper indicates $Cl^-$ or $Br^-$; $I^-$ and $F^-$ do not respond to the test. Interfering anions are those that give dark or highly coloured compounds with Ag (*e.g.*, sulphide, chromate). R. E. ESSERY

3498. **Micro-determination of chloride by non-aqueous potentiometric titration.** D. T. Lefferts (Colgate-Palmolive Co., Jersey City, N.J., U.S.A.). *Microchem. J.*, 1958, **2** (2), 257–261.—The anhydrous character of glacial acetic acid together with its ability to sharpen the end-point of the potentiometric curve make it a suitable medium for the direct argentimetric titration of $Cl^-$ with a silver - glass electrode system and a pH meter. The method described permits the titration with 0·003 *N* $AgNO_3$ of 0·4 to 5·0 mg of $Cl^-$ in 25 to 150 ml of glacial acetic acid. D. F. PHILLIPS

3499. **Rapid constant-current potentiometric titration of chloride ion. Use of polarisable platinum electrodes.** R. W. Freedman (Consolidation Coal Co., Res. and Devel. Div., Library, Pa., U.S.A.). *Anal. Chem.*, 1959, **31** (2), 214.—The method described has been developed for determining $Cl^-$ in water-soluble and oil-soluble organic materials. It can be used to determine any ion that yields silver salts of low solubility under standard conditions. K. A. PROCTOR

3500. **Spectrophotometric determination of microgram quantities of chloride and fluoride in metal oxides, salts and solutions.** B. D. La Mont and B. W. Conroy (Westinghouse Electric Corp., Atomic Power Dept., Pittsburgh). *U.S. Atomic Energy Comm.*, Rep. WCAP-918, 1958, 19 pp.—Nuclear power reactors and high-pressure boilers constructed of stainless steel are subject to stress corrosion in the presence of $F^-$ and $Cl^-$ in oxygenated systems. Consequently, determinations are made for $Cl^-$ (0·5 to 15 μg) and $F^-$ (0·5 to 50 μg). A procedure involving bleaching of the mercury - diphenylcarbazone complex is used to determine the $Cl^-$. Fluoride is measured by the bleaching of the thorium - thoron complex. These procedures were successfully applied to samples of metal oxides, salts and solutions. NUCL. SCI. ABSTR.

3501. **Quantitative determination of perchlorate ion in solution.** G. M. Nabar and C. R. Ramachandran (Dept. of Chem. Technol., Univ. of Bombay, India). *Anal. Chem.*, 1959, **31** (2), 263–265.—The method is based on the reaction between a known excess of methylene blue (**I**) and a soluble perchlorate. Sparingly soluble methylene blue perchlorate (**II**) is formed and is removed by filtration. The excess of **I** is determined colorimetrically in the filtrate. The small amount of **II** which is dissolved introduces a constant error, for which a correction is applied. Interference is caused by the presence of $Cr_2O_7^{2-}$, $SO_4^{2-}$, $MnO_4^-$, $MoO_4^{2-}$ and $IO_4^-$, since these anions form ppt. with **I**. F. L. SELFE

3502. **Determination of bromate and periodate in the presence of each other.** L. Szekeres (Chem. Inst., Agric. Univ., Budapest, Hungary). *Z. anal. Chem.*, 1959, **165** (1), 32–36.—Two methods of determining $BrO_3^-$ and $IO_4^-$ in mixtures are developed. First, the sum of the two anions is determined iodimetrically in an aliquot. In one method (*a*), the anions are then reduced with HBr, $BrO_3^-$ giving elementary Br, and $IO_4^-$ giving IO The Br is converted into $Br^-$ (alkaline urea $H_2O_2$) and the remaining $IO_3^-$ are determined w $Na_2S_2O_3$. This method is preferred for low con of $BrO_3^-$. In the other method (*b*), $IO_4^-$ reduced with aq. $H_2O_2$ - $NaHCO_3$ to $IO_3^-$, the exc of $H_2O_2$ is destroyed, and $BrO_3^-$ plus $IO_3^-$ determined with $Na_2S_2O_3$. This method is prefer for low concn. of $IO_4^-$. Results accurate to wit ±1% are obtained for mixtures containing 5 30 ml of 0·1 *N* $KIO_4$ and 5 to 30 ml of 0·1 *N* KBr J. P. STERN

3503. **Inhibition of the catalytic effect of iodi on the system ceric sulphate - arsenous acid.** R. Magee and H. Spitzy (Paracelsus Inst., Bad Ha Austria). *Mikrochim. Acta*, 1959, (1), 101–106. Quadrivalent Ce gives a stable colour with bruci acetate in $H_2SO_4$ soln. only after development 10 to 12 min. at 105°. The application of t reaction to the micro-determination of iodine blood serum by means of its inhibitory effect on t $Ce(SO_4)_2$ - $As_2O_3$ reaction (*cf.* Spitzy *et al.*, *An Abstr.*, 1959, **6**, 658) introduces undesirable comp cations. T. R. ANDREW

3504. **Chelometric analysis of manganese - ma nesium and manganese - magnesium - zinc mixtur Fluoride ion as a demasking agent.** W. G. Scribn (Res. and Engng Div., Monsanto Chemical C Dayton, Ohio, U.S.A.). *Anal. Chem.*, 1959, (2), 273–275.—The fluoride ion demasks Mg sele ively from a mixture of the chelates of Mn, Mg a Zn with EDTA. This makes possible a rap analysis of Mn - Mg and of Mn - Mg - Zn mixtur as required in the analysis of ferrites. *Procedure* Dissolve the ferrite sample in HCl. Remove by extraction of Fe cupferrate into benzen *iso*amyl alcohol (1:1). Separate the aq. phas add hydroxyammonium chloride (0·2 g) and adj the pH to 10 with aq. $NH_3$ soln. (1:1). A Eriochrome black T - NaCl (1:200), warm to 4 and titrate with standard EDTA soln. (disodiu salt). The titration gives total bivalent metal io After the end-point, add 2 to 3 g of solid NaF a stir for 1 min. From a burette, add standard M soln., 1 ml at a time, until a permanent red colo is obtained. Stir for 1 min. and titrate the exc of Mn with standard EDTA soln. The amount standard Mn soln. equivalent to the Mg present thus obtained. After the second end-point, Zn is present, add KCN (2 ml of a 10% soln. every millimole of Zn) to displace Zn from chelate. From a burette add an excess of standa Mn soln., then titrate the excess of Mn with standa EDTA soln. Calculate the Zn content of the mi ture. The Mn content of the original sample obtained by difference. The analysis of a terna mixture can be completed in <40 min., includi calculations. The error is generally <0·1 mg each metal. Extensions of the method to oth metal combinations are suggested. F. L. SELFE

3505. **Co-precipitation and ion-exchange adso tion of technetium.** Niro Matsuura, Masuo Koji and Akira Iguchi (Fac. of Gen. Educ., Tokyo Uni Komaba, Meguro-ku). *Japan Analyst*, 1958, (12), 792–794.—Co-pptn. of Tc in the form $KTcO_4$ was examined with CuS, CdS, FeS a $As_2S_3$. Co-pptn. with CuS from 0·3 *N* HCl appe to be the best method for the collection of In $HNO_3$ or $HClO_4$ soln., a mono - monoval adsorption is observed with Dowex 1X-8

mesh). Technetium seems to be adsorbed as $ClO_4$, most of which is readily eluted with 0·5 *M* $HClO_4$, a small residual amount of Tc being only slowly eluted. K. Saito

506. **Spectrophotometric determination of perhenate.** J. B. Headridge (Chem. Dept., Univ., ffield, England). *Analyst*, 1958, **83**, 690–691.—a proposed method for the determination of nium in organic rhenium complexes containing the samples are oxidised by fusion with $Na_2O_2$ a micro Parr bomb and the final acidified soln. tains Na, H, $Cl^-$, $NO_3^-$ and perrhenate ions. determination of perrhenate, the u.v. spectrum potassium perrhenate in the presence of other s was investigated. The molar extinction coeff. 3610 at 228 m$\mu$ and 6060 at 206 m$\mu$. Apprecle absorption by $Cl^-$ starts only below 210 m$\mu$; $_3^-$ has an absorption peak at 303 m$\mu$ and a imum at 264 m$\mu$. The absorption peak at 3 m$\mu$ can be used for the determination of rhenate in soln. containing no other ions that orb appreciably at this wavelength, and the t of linear extinction *vs.* concn. over the range o 50 p.p.m. of Re passes through the origin. e optimum wavelength for the determination in presence of both $Cl^-$ and $NO_3^-$ is 258 m$\mu$ over range 0 to 250 p.p.m. of Re in a 0·65 *M* soln. of Cl. The intercept of this graph on the extinction s represents the slight absorption of the NaCl. th application of the appropriate corrections for and $NO_3^-$, this method provides a rapid means determining perrhenate in simple soln.

A. O. Jones

3507. **Volumetric determination of iron(III) with droxylamine as reducing agent.** G. Gopala Rao d G. Somidevamma (Andhra Univ., Waltair, dia). *Z. anal. Chem.*, 1959, **165** (6), 432–436 English).—Ferric iron is reduced to $Fe^{2+}$ with cess of hydroxylamine at an acidity of 0·2 to *N* with respect to $H_2SO_4$ and at a temp. of 100°. e soln. is cooled, the acidity is made 6 *N*, and the $^{2+}$ are titrated with sodium vanadate soln., th N-phenylanthranilic acid as internal indicator. e precision is within $\pm$0·2%. G. P. Cook

3508. **Photometric determination of iron(III) ploying 1:2-diamino*cyclo*hexanetetra-acetic acid.** Bermejo Martinez and R. Rey Mendoza (Univ. of ntiago de Compostela, Spain). *Chemist Analyst*, 58, **47** (4), 94–95.—Prepare a 5% aq. soln. of 2-diamino*cyclo*hexanetetra-acetic acid by disving the acid in the required amount of NaOH n. and neutralising with HCl, or by using the odium salt. Into a 25-ml flask place an aliquot the sample soln. such that the final concentration Fe will be in the range 30 to 250 $\mu$g per ml, and l 3 ml of reagent soln., followed by 2 *M* NaOH op by drop till pH 4 is reached (pH meter or licator paper). Dilute to 25 ml, mix, and measthe absorption in a photo-electric colorimeter ainst a water blank, using an indigo filter. fer results to a standard curve. Cations that m coloured complexes with the reagent ($Cu^{II}$, $^{II}$, $Mn^{II}$ and $Co^{II}$) interfere. At pH 4, the colour stable to light for at least 10 days. A small cess of reagent does not interfere, but a large cess should be avoided, owing to the limited ubility of the free acid at pH 4.

R. E. Essery

3509. **Spectrophotometric study of the cyanomalonate ion. Application to the spectrophotometric determination of the ferric ion.** G. Mignonac, R. Miquel and C. Bonnemaison (Lab. de Chim. Gén., Fac. des Sci., Toulouse, France). *Bull. Soc. Chim. France*, 1958, (11–12), 1323–1330.—Diethyl cyanomalonate (**I**) is prepared by the action of ClCN on diethyl sodiomalonate. Its absorption spectrum in the u.v. (max. at 214 and 247 m$\mu$) at various pH values is measured and the p*K* shown to be 1·3. When **I** is caused to react with $Fe^{3+}$ at pH 2·8 to 3·8 and extracted with $CHCl_3$, a complex with max. at 504 m$\mu$ and absorption coeff. of 3600 is obtained. The nature of the complexes with $Fe^{3+}$ is investigated and by pptn. in aq. soln. a complex approximating to $X_2FeOH$ (X = **I**) is obtained. By extraction in $CHCl_3$, complexes with compositions $FeX_3$ and $FeX_4H$ are obtained. *Procedure for determination of $Fe^{2+}$ and $Fe^{3+}$ simultaneously*—An acid soln. of the two ions is adjusted to pH 3 to 4 with Na acetate and then a slight excess of a reagent, consisting of 1:10-phenanthroline (0·2 g), 0·1 *M* diethyl ammoniocyanomalonate (**II**) (5 ml), glacial acetic acid (5 ml) and water to 25 ml, is added. The $Fe^{3+}$ complex is extracted with $CHCl_3$ and measured spectrophotometrically, and the $Fe^{2+}$ complex with 1:10-phenanthroline is measured similarly in the aq. layer. This gives low results for $Fe^{3+}$ with a relative error of $<5\%$. *For determination of $Fe^{3+}$*—To a sample of $Fe^{3+}$ (0·7 to 11 $\mu$g) at pH 2·8 to 4 is added a slight excess of 0·1 *M* **II** (at least 4 molar proportions), and after a few minutes the complex is extracted into $CHCl_3$ and the absorption measured (with a filter, between 460 and 520 m$\mu$). A similar semi-micro method is described. E. J. H. Birch

3510. **Polarographic determination of iron and manganese in ores and metallurgical products.** I. M. Issa, R. M. Issa and I. F. Hewaidy (Dept. of Chem., Univ. of Egypt, Giza). *Chemist Analyst*, 1958, **47** (4), 88–90.—In the polarographic determination of Mn in triethanolamine, the use of $Na_2SO_3$ to remove dissolved O and excess of $H_2O_2$ (used as an oxidant) permits Fe and Mn to be determined in the same soln. Transfer the soln. containing Fe and Mn to a 25-ml flask containing 8 ml of 50% triethanolamine. Add sufficient 5 *M* NaOH to make the soln. 0·5 *M* when diluted to the mark. Add a little water and bubble air for 5 to 10 min., or add a few drops of $H_2O_2$ and mix. Dilute to 25 ml, transfer 10 ml to the polarograph cell, and bubble N for 15 min. If $H_2O_2$ has been used, set aside for 30 min., or add 0·2 g of $Na_2SO_3$. Record the polarogram, read the diffusion currents for the first and second waves, and refer results to standard curves for Fe and Mn, respectively. For the determination of Mn in steel or cast iron, 1 g of sample is dissolved in 10 ml of 50% $HNO_3$, the soln. is filtered, filtrate and washings are made up to 100 ml and 10 ml is treated as described above, only the Mn wave being recorded. For Fe and Mn in ores, 1 g is dissolved in 50% $HNO_3$ with a little $H_2O_2$, the soln. is fumed with $H_2SO_4$, diluted with water, filtered, and made up to 250 ml, 10 ml being treated as described above. Results agree well with those by classical methods. R. E. Essery

3511. **Determination of metallic iron, iron oxides, iron carbide and free carbon in iron catalyst treated with carbon monoxide.** Yoshio Murata and Shigeaki Kasaoka (Fac. of Educ., Univ. of Osaka Prefecture, Sakai). *Japan Analyst*, 1958, **7** (11),

721–724.—Total carbon is determined by the combustion method (*cf.* Touhey and Redmond, *Anal. Chem.*, 1948, **20**, 202). The sample (300 mg) is boiled with $H_2SO_4$ (1:10, 100 ml) for 30 min., then filtered, and the residue is dried and used for the determination of free carbon by the combustion method. Total iron and ferrous iron are determined by the mercuric chloride - iodine method (*cf. Anal. Abstr.*, 1956, **3**, 3049; 1958, **5**, 3743). K. Saito

3512. **Combustion method for determination of sulphur in ferrous alloys. Modifications for minimising errors.** J. W. Fulton and R. E. Fryxell (Transformer Div., General Electric Co., Pittsfield, Mass., U.S.A.). *Anal. Chem.*, 1959, **31** (3), 401–405.—Losses in the combustion method for determining S in metals have been studied by the use of $^{35}S$. Above 1550°, only 1 to 2% of the total S remains in the slag; most of the loss occurs by adsorption on the glassware of the delivery system. A further loss is due to formation of $SO_3$, which is not titrated by $KIO_3$. By using a temp. of 1550°, a shortened delivery system, and an O flow of 5 litres per min., results of 92% of the theoretical are obtained when the gases are absorbed in $H_2O_2$, rinsings from the delivery system added, and the whole titrated with NaOH soln. to a bromocresol purple end-point. The value as titrated times a loss factor of 1·09 gives good precision and accuracy over the range 0·01 to 0·272%. For S contents $> 0{\cdot}01\%$, rinsings and blank may be ignored.

P. D. Parr-Richard

3513. **4:4′-Substituted 2:2′-dipyridyls in chelation reactions with ferrous iron.** G. F. Smith and W. M. Banick, jun. (Noyes Chem. Lab., Univ. of Illinois, Urbana, U.S.A.). *Analyst*, 1958, **83**, 661–666.—The mol. extinction coeff. and wavelengths of max. absorption have been determined for the $Fe^{2+}$ complexes of eleven 4:4′-derivatives of 2:2′-dipyridyl, *viz*, those with $-CH_3$ (**I**), $-C_2H_5$ (**II**), –Br (**III**), –Cl (**IV**), $-OCH_3$ (**V**), $-OC_2H_5$ (**VI**), $-OC_6H_5$ (**VII**), $-COOC_2H_5$ (**VIII**), $-CONH_2$ (**IX**), –COOH (**X**) and $-NO_2$ (**XI**) as substituents. Procedures for ascertaining the optimum pH for formation of the chelate complexes and their extraction are described. The spectrophotometric data assign the reagents to 3 groups, *viz*, unsubstituted 2:2′-dipyridyl and ligands **I**, **II**, **III** and **IV**; **V**, **VI** and **VII**; and **VIII**, **IX** and **X**. As with the $Fe^{2+}$ complexes of the 1:10-phenanthrolines, attempts to use the u.v. absorption for determination of Fe failed owing to interference from the necessary excess of ligand present. In certain circumstances it might be possible to use ligands **II**, **VI**, **VII** and **VIII** (and 4:4′-diphenyl-2:2′-dipyridyl), which absorb negligibly at 340, 330, 340 and 350 (and 356 mμ), respectively, whereas their respective Fe complexes absorb at 355, 359, 363 and 384 (and 386 mμ). All the $Fe^{2+}$ complexes as well as the excess of ligand are extractable. This restricts their use in analysis except in special circumstances.

A. O. Jones

3514. **Direct titration of ferricyanide in the presence of zinc sulphate. Determination of nitrite.** B. R. Sant (Coates Chem. Lab., Louisiana State Univ., Baton Rouge, U.S.A.). *Anal. Chim. Acta*, 1958, **19** (6), 523–524.—Potassium ferricyanide soln. (*M*) heated to boiling in the presence of $Zn^{2+}$ may be quant. titrated with $NO_2^-$, at a pH of 6 to 7, or in soln. of higher alkalinity up to abo 0·3 *N* NaOH. The end-point is shown by comple decolorisation of the soln. The method may used for the determination of $NO_2^-$.

T. R. Andrew

3515. **Proximate method of spectral analysis austenitic steel.** A. G. Komarovskiĭ. *Tse Nauch.-Issled. Inst. Tekhnol. i Mashin.*, 1957, **8** 199–225.—The effect of a third metal on t spectroscopic analysis was studied in spark, arc a a.c. arc discharges of binary alloys of Fe with S Mn, Cr, Ni, Mo, W, Ti, V, Co, Al, B and Nb and complex high-alloyed steels. The results we plotted on log ($I_p/I_1$) and log *C* co-ordinates, whe $I_p$ and $I_1$ are the line intensities of the eleme sought and the comparison element (Fe) and *C* the concn. (wt. %) of the element sought. T regularity of the principle of the parallel shift of t calibration lines caused by the presence of the thi element was established for different types of ste The coeff. of parallel shift classified the metals in a few groups, reducing the number of standar needed. The accuracy of determination of a element was within 2·5 to 5·1% and the analys was completed within 10 min. Working curves all elements and tables of line-pairs of spectral lin are given. The processes within the clouds of t spark affected by the duration ("effect of firing were investigated. Only the determination of M Cr, Al and Nb was affected by the "effect of firing Analyses in atmospheres of air, N and O showed th this effect was due to oxidation. Chem. Abstr.

3516. **Rapid determination of various non-metall inclusions in steel.** Takuho Ikegami and Ohi Kammori (Tech. Res. Inst., Yawata Iron and Ste Works, Fukuoka-ken). *Japan Analyst*, 1958, (10), 636–640.—In order to minimise the time take for electrolysis, the amount of the sample is reduce to 10 g and the non-metallic inclusions are fused wi $Na_2CO_3$ (3 g); the melt is dissolved in water (50 m and made acid with $H_2SO_4$ (1:5, 15 ml) and a fe drops of 10% hydroxyammonium sulphate sol The insol. residue is fused with $K_2S_2O_7$ and the dissolved in dil. $H_2SO_4$. The combined soln. a made up to 250 ml and the following components a determined colorimetrically with the followi reagents—Si with $(NH_4)_2MoO_4$; Al with alumin (Cr and Fe being removed by mercury catho electrolysis); Fe with nitroso-R salt; Mn wi $(NH_4)_2S_2O_8$; Ti with $H_2O_2$; Cr with diphenylcar azide. K. Saito

3517. **Hydrogen in steel.** B. A. Shmelev. *Tse Nauch.-Issled. Inst. Tekhnol. i Mashin.*, 1957, **8** 12–40.—Methods of determining H in steel a discussed and a method of sampling and stori specimens is outlined. The molten metal is dra into quartz tubes (8 to 9 mm inside diam.), co stricted every 20 to 25 mm. After quenching water the tube is broken at the constrictions and t specimens are stored under glycerol. Hydrogen determined by electrolytic saturation in two ce in series, with the specimen as a cathode in one a a platinum wire in the other. The H absorbed measured by the difference in vol. of displac electrolyte in both cells. After saturation, t specimen is stored in glycerol and the H evolved ageing is determined by the vol. of glycerol d placed. The specimen is then analysed for *in vacuo*. Chem. Abstr

3518. **Hydrogen in ferrosilicon. Analytical method and average hydrogen contents of some commercial grades.** N. Christensen and K. Gjermund-. *J. Iron St. Inst.*, 1958, **190** (3), 248–254.—e presence of hydrated lime and alumina was nd to give severe segregation of H, and the content increased with decreasing particle size the sample, increasing exposure to air and idity of analysis after manufacture. The itations of the vacuum-fusion procedure are cussed. J. W. O. Pyemont

3519. **Spectrophotometric determination of magnesium in cast iron with xylidyl blue.** Takuho egami, Ohiko Kammori and Takayuki Jitsumatsu ech. Res. Inst., Yawata Iron and Steel Works, kuoka-ken). *Japan Analyst*, 1958, **7** (10), 641–4.—Mann and Yoe's colorimetric determination Mg with xylidyl blue (**I**) (*cf. Anal. Abstr.*, 1956, 2009) was applied to the rapid (90 min.) analysis cast iron. There is no interference from $< 80 \mu g$ Al, Ti, As, Mn and Ca, which remain in soln. er the electrolytic separation of Fe with a mercury thode. The excess of $H_2SO_4$ is removed by heat-; $HClO_4$ can be used in its place. *Procedure*—ssolve the sample (0·1 g) in $H_2SO_4$ (1 : 9, 5 ml) d $H_2O_2$ (15%, 10 ml), boil, filter off and wash the t. with $H_2SO_4$ (1 : 100) and remove Fe from the rate by electrolysis with a mercury cathode. aporate the soln. until white fumes cease to pear. Dissolve the residue in 100 ml of water and a 5-ml aliquot add **I** (0·015% in ethanol, 5 ml) d $Na_2B_4O_7$ soln. (0·08 *M*, 0·5 ml) and dilute 25 ml with water. Measure the extinction at 0 m$\mu$, with a reference soln. containing the same ounts of **I** and $Na_2B_4O_7$. K. Saito

3520. **Quick method for the determination of lead steel.** S. Meyer and O. G. Othmar (Neunkircher senwerk A.-G., Neunkirchen, Saar). *Arch. senhüttenw.*, 1958, **29** (11), 677–681.—Three pid methods are developed in which Pb is parated as $PbSO_4$, or gravimetrically determined $PbMoO_4$ or $PbCrO_4$. With the first method ults are obtained within 2 to 2·5 hr., the mean or being $\simeq 0{\cdot}001\%$ for 0·2% of Pb. Photometric terminations were also found to be suitable. The is directly determined in the test soln. as $PbI_2$. ngle determinations can be made in 45 min., th a standard deviation of $\pm 0{\cdot}003$ for contents Pb of $\simeq 0{\cdot}2\%$. L. M. Riegelhaupt

3521. **Effect of temperature on the spectrophotometric determination of phosphorus in iron and steel by the molybdovanadophosphate method.** Hiroshi tagawa and Norio Shibata (Hitachi Cent. Res. b., Kokubunji, Tokyo). *Japan Analyst*, 1958, (12), 788–789.—The temperature coeff. of the tinction of molybdovanadophosphate in $HClO_4$ n. (*cf.* Baghurst and Norman, *Anal. Abstr.*, 56, **3**, 82) is markedly decreased by the addition ethanol (15 ml per 100 ml of the final soln.) or $_2SO_4$ (2 g). K. Saito

3522. **Methods for the analysis of steel. Part 9. osphorus in high chromium - nickel steels.** British ndards Institution (2 Park Street, London). 5. 1121: Part 9: 1948, incorporating amendment vember, 1957, 9 pp.—The original method was veloped for use on high Cr - Ni steels and other hly alloyed steels and depended on the oxidation he Cr in soln. by fuming with $HClO_4$ for 10 min., owed by reduction with HBr. Phosphorus is d. from cold soln. with nitromolybdate and the ppt. is converted into $PbMoO_4$, which is weighed. The amendment provides for the determination of P in all steels by raising the fuming temperature until $HClO_4$ refluxes on the walls of the beaker for 10 to 15 min. The subsequent procedure is unaltered. J. O. Lay

3523. **Removal of sulphuric acid from phosphoric acid used for the determination of sulphur in high-chromium steel.** Hiroshi Kitagawa and Norio Shibata (Hitachi Central Res. Lab., Kokubunji, Tokyo). *Japan Analyst*, 1958, **7** (9), 587–588.—Sulphuric acid in commercial $H_3PO_4$ (sp. gr. 1·7) is readily removed by heating with metallic chromium (0·2 g for 10 ml of $H_3PO_4$) at $>250°$ for 30 min. and does not then increase the blank value for the determination of S by the $H_2S$ method. Sulphuric acid is also satisfactorily removed by the tin - phosphoric acid method (*cf.* Kiba *et al.*, *Anal. Abstr.*, 1956, **3**, 2708; Kiba and Kishi, *Ibid.*, 1957, **4**, 3305). K. Saito

3524. **The oxidation of chromium [in steel] with perchloric - phosphoric acid. A study by the Box - Wilson method.** Hiroshi Kitagawa and Norio Shibata (Hitachi Central Res. Lab., Kokubunji, Tokyo). *Japan Analyst*, 1958, **7** (10), 619–623.—Optimum conditions for the oxidation of Cr in low-alloy steel with $HClO_4$ and $H_3PO_4$ were studied by the Box - Wilson statistical method (*J. R. Statist. Soc., B*, 1951, **13**, 1), and were found to be—ratio of $H_3PO_4$ to $HClO_4$, $0{\cdot}4 \pm 0{\cdot}05\%$ (v/v); temp., 203° $\pm$ 1°; time of oxidation, $3{\cdot}5 \pm 0{\cdot}5$ min. For the reduction of simultaneously oxidised Mn, $NaN_3$ (Willard and Young, *J. Amer. Chem. Soc.*, 1929, **51**, 139) is the best reductant. *Procedure for low-alloy steel*—Dissolve the sample (0·2 to 1 g) in mixed acid ($HClO_4$, 500 ml; $H_3PO_4$, 200 ml; $HNO_3$, 100 ml; and water, 200 ml) (20 to 40 ml), heat at 202° to 204° for 3 to 4 min., dilute fourfold, boil with $NaN_3$ soln. (2%, 0·1 to 0·5 ml) and titrate with 0·033 *N* $FeSO_4$ and $KMnO_4$ by the usual method. K. Saito

3525. **Photometric determination of manganese in steel and cast iron.** J. E. Bolzan (Lab. Quim.-Metalurg., Ferrocarril General Roca, Remedios de Escalada, Argentina). *Chemist Analyst*, 1958, **47** (4), 95–96.—The modified persulphate - silver method eliminates the error due to foreign ions by using a bleached blank. Dissolve the sample (50 mg) in 5 ml of acid mixture (150 ml of conc. $H_2SO_4$, 150 ml of conc. $H_3PO_4$, 700 ml of water) by heating in a glycerol bath. When dissolution is complete, oxidise with a few drops of conc. $HNO_3$ and heat to expel nitrous fumes. With cast iron, dilute to reduce the acidity and filter off the graphite. Then add 2 ml of 1% $AgNO_3$ soln. and 2 ml of satd. $(NH_4)_2S_2O_8$ soln., boil for 2 to 3 min. in a glycerol bath to expel oxygen, then cool rapidly in tap water and make up to 25 ml. Read the absorption in a test-tube cell against water, in a colorimeter with a logarithmic scale, and with a green filter. Add to the cell 1 to 2 drops of 0·3% $H_2O_2$ to bleach the permanganate, and read the absorption due to other ions. All cells should be matched to a position of min. absorption with water, and the sample should be analysed concurrently with a similar material of known Mn content. The total permanganate reading, corrected for the bleached blank, is proportional to the Mn content. Recoveries from a standard cast iron and 4 standard steels were satisfactory. R. E. Essery

3526. **Determination of low cobalt contents in ores, pig iron and steel.** G. Graue, S. Eckhard and W. Gradtke (Phoenix-Rheinrohr A.-G., Duisburg-Ruhrort, Germany). *Angew. Chem.*, 1959, **71** (1), 28–30.—The high neutron-capture cross-area of Co necessitates the accurate determination of small quantities of Co in materials to be subjected to irradiation. This is best done photometrically with nitroso-R salt. Iron interferes and is removed by extraction into di*iso*propyl ether as $FeCl_3$ or preferably by pptn. as basic oxide with ZnO (which also removes Cr, W, Mo, Ta, Ti, Nb, Zr, V and Cu). High accuracy is attained with Co contents of the order of 0·001 to 0·1%. Manganese causes low, and Cu high, results, and Cr interferes. Two methods are described. (*i*) Dissolve the sample (1 g) in HCl (1:1) (20 ml), oxidise with $KClO_3$ (1 g), evaporate to dryness, and dissolve the residue in HCl (3:1) (20 ml). If >0·5% of Si is present, filter. Concentrate to 20 ml, and extract with di*iso*propyl ether (4 × 30 ml). Evaporate the Fe-free aq. phase to dryness, dissolve in $HNO_3$ (2 ml), evaporate just to dryness, dissolve in $HNO_3$ (1:1) (10 ml), and add Na citrate - NaOH buffer at pH 6 to 6·5. Dilute to 50 ml, filter, treat 25 ml of the filtrate with 0·5% nitroso-R salt soln. (5 ml) and after 10 min. add $HNO_3$ (1:2) (5 ml). Dilute to 50 ml, shake, and measure the colour photometrically against a blank. Read the Co content from a calibration curve. (*ii*) Dissolve the sample (1 g) in $HNO_3$ (1:1) (10 ml), boil off N oxides, add $H_2O_2$ (1:1) (3 ml), boil for 2 min., dilute to 30 ml with $H_2O$, and add a suspension of ZnO (5 g). Boil briefly, dilute to 100 ml, shake, and filter. Determine the Co content of 50 ml of filtrate as described above, with a mercury lamp and a filter (Hg 546). Nickel (>2%) interferes. J. P. Stern

3527. **Determination of cobalt with 2-nitroso-1-naphthol.** H. Schüller (Landwirtschaftl.-Chem. Bundesversuchsanst., Vienna). *Mikrochim. Acta*, 1959, (1), 107–121.—The 'cold' procedure of Claassen and Daamen (*cf. Anal. Abstr.*, 1955, **2**, 3366) is preferred to the 'hot' procedure of Baron (*cf. Anal. Abstr.*, 1954, **1**, 489) since the interference of Mn can be readily eliminated in the former procedure. In the examination of agricultural material, platinum from laboratory ware acts as a contaminant. Four procedures are described for overcoming interference due to Pt—(*i*) ion-exchange separation of Pt as chloroplatinate on Dowex 2-X8 anion-exchange resin in 6 *N* HCl; (*ii*) extraction of $Pt^{2+}$ with diphenylthiocarbazone at pH 1 to 2; (*iii*) a combined extraction and ion-exchange procedure applicable in the presence of large amounts of phosphate and inorganic salts; (*iv*) a 'correction' procedure by which the Co content may be deduced from measurements of the extinctions at 365 and 420 mμ without prior separation of Pt.
T. R. Andrew

3528. **Spectrophotometric determination of cobalt with 1-(2-pyridylazo)-2-naphthol.** G. Goldstein, D. L. Manning and O. Menis (Anal. Chem. Div., Oak Ridge Nat. Lab., Tenn., U.S.A.). *Anal. Chem.*, 1959, **31** (2), 192–195.—The $Co^{3+}$ chelate with 1-(2-pyridylazo)-2-naphthol is readily extracted into $CHCl_3$, the extract showing absorption peaks at 590 and 640 mμ. Fewer interferences are encountered when the extinction is measured at 640 mμ. Beer's law is obeyed over a range of 0·1 to 2·4 μg of Co per ml, with a coefficient of variation ≃3%. Interfering ions are $Cu^{2+}$ (when Cu:Co > 1:1), $Ni^{2+}$ (Ni:Co > 10:1), and $Fe^{3+}$, $Zn^{2+}$ and $Cd^{2+}$ (milligram amounts). Lesse amounts of these ions are readily masked by citrat A procedure is given for the determination of Co i concn. from 0·1 to 10 p.p.m. in impure thoriu oxide, and it is suggested that the method may als be applied to the determination of Co in steel an other alloys. A strong base anion-exchange resi is used to concentrate the Co and to separate it fro Th and from interfering ions. In this separatio Co is adsorbed from a soln. 10 *M* with respect t HCl and is eluted with 4 *M* HCl. F. L. Selfe

3529. **Co-precipitation of cobalt(II) with zin sulphide.** Hiroshi Hamaguchi and Toshi Kawa shima (Chem. Dept., Tokyo Univ. of Educ., Koish kawa). *Japan Analyst*, 1958, **7** (10), 627–630.— Co-precipitation of $Co^{II}$ with ZnS (investigated wit $^{60}Co$ as tracer) is largely affected by the rate of flo of $H_2S$. At pH 2·5 only 0·5% of Co (≃0·02 M soln.) is co-pptd. when the rate of flow is <10 m per min., whilst ≃25% of Co is co-pptd. when th flow rate is 200 ml per min. The use of thioacet amide (*cf.* Swift and Butler, *Anal. Abstr.*, 1956, 3 2061) does not prevent the co-pptn. K. Saito

3530. **Use of diphenylglyoxime in the photometri determination of nickel.** Z. Gregorowicz (Inst. Anorg. Chem. d. Schlesischen Tech. Hochsch Gliwice, Poland). *Acta Chim. Acad. Sci. Hung* 1959, **18** (1–4), 79–84 (in German).—Dipheny glyoxime (**I**) is particularly useful for the dete mination of Ni in soln. containing ethanol, whe dimethylglyoxime cannot be used. To the nick soln. in a 50-ml flask are added 5 ml of poly(viny alcohol) soln. (0·5% aq.), 6 ml of **I** soln. (0·02% i ethanol), 8 ml of satd. aq. iodine soln. and a fe drops of 2 *N* aq. $NH_3$ soln. After being shaken fo 2 min., the soln. is made up to volume and th colour is measured, a Pulfrich photometer wit Zeiss S filters and 5-cm cells being used. A suitab range of concn. is 0·01 to 0·10 mg of $Ni^{2+}$ per 50 m
H. M.

3531. **Gasometric determination of metallic nick in the presence of nickel(II) oxide.** E. Krejca (Res. Inst. Fats and Oils, Prague). *Chem. List* 1958, **52** (12), 2410–2411.—The vol. of H liberate by dissolving a mixture of metallic nickel and Ni in acid, which is equiv. to the amount of metall Ni, can be measured in a special apparatus (illu strated); in the upper part the vol. of H is measure and the lower part serves for the reduction of Ni and for the dissolution of the reduced Ni.
J. Zýka

3532. **Analysis of nickel sulphamate platin solutions.** G. H. Bush and D. C. Higgs (Armamer Res. and Devel. Estab., Fort Halstead, nr. Seve oaks, Kent, England). *Trans. Inst. Met. Finish* 1958–59, **36** (2), 43–47.—Examination of th effects of process variables on the physical properti of deposits of Ni from nickel sulphamate baths described. Synthetic soln. of known compositio were used. Determination of N by the Kjelda method showed that no catalyst was necessary $NH_4^+$ were determined by distillation of an aliqu of the bath made alkaline with NaOH. Dire titration with EDTA (disodium salt), with murexi as indicator, was used for determining Ni. Bor acid was determined by titration with NaOH soln in the presence of mannitol, after separation fro Ni by passage through a cation-exchange colum

aphthalene-1:3:6-trisulphonic acid was deter-ned by measurement of the extinction of a diluted n. at 280 mμ. Chloride was determined by the olhard method after removal of Ni by means of an -exchange column. The method of calculating e results is given and the results are tabulated.
C. H. Cowper-Coles

3533. **Reduction of nickel(IV) dimethylglyoximate.** Okáč and M. Šimek (Inst. Anal. Chem., asaryk Univ., Brno, Czechoslovakia). *Chem. sty*, 1958, **52** (12), 2285–2291.—The stability of l soln. of oxidised Ni dimethylglyoximate scribed previously (*Chem. Listy*, 1958, **52**, 1903) s been studied potentiometrically and photo-etrically, with the use of various agents for the idation of dimethylglyoxime [bromine, iodine, $Fe(CN)_6$ and O, in alkaline and aq. $NH_3$ soln.] d for the reduction of the reaction product tration with $SnCl_2$). The red complex $[NiD_3]^{2-}$ is duced to the yellow soln. of the bivalent Ni mplex $[NiD_3]^{4-}$; both complexes are stable only strongly alkaline soln., the latter only in an ert atmosphere. When neutralising alkaline n., the salt of dimethylglyoxime $Ni(DH)_2$ is rmed. The oxidation of Ni dimethylglyoximate alkaline soln. to the red form must be carried out alkaline soln. containing an excess of dimethyl-yoxime.
J. Zýka

3534. **Spectrophotometric determination of ruth-ium.** R. P. Larsen and L. E. Ross (Chem. Engng v., Argonne Nat. Lab., Lemont, Ill., U.S.A.). *al. Chem.*, 1959, **31** (2), 176–178.—Ruthenium is termined as perruthenate. Ruthenium tetroxide distilled from a 6 *N* $H_2SO_4$ soln., containing 40 to 0 μg of Ru, in the presence of sodium bismuthate 5 g) as oxidant. The distillate is collected in -cold *N* NaOH containing NaClO (1 ml of 5% ln.). Distillation is complete in $<5$ min. The ceiver is then warmed to room temp. and the soln. luted to a known vol. with *N* NaOH. The tinction of the soln. is measured at 385 mμ ainst a reagent blank. Calibration must be ecked daily. If this is done, a precision, at the % confidence level, of $\pm 1{\cdot}5\%$ with a max. viation of 2·0% is shown by 12 replicate deter-nations. The procedure has been applied to the termination of up to 5% of Ru in uranium-thenium alloys.
F. L. Selfe

3535. **Use of oscillographic polarography in antitative analysis. IX. Identification and termination of rhodium in the presence of plati-m, palladium and gold.** P. Beran and J. Doležal nst. Anal. Chem., Charles' Univ., Prague). *em. Listy*, 1958, **52** (12), 2403–2404.—The nsitive oscillographic determination of Rh in atinum, palladium and gold is based on the talytic effect of $Rh^{3+}$ (*Chem. Listy*, 1957, **51**, 1289). ie depolarisation of $Rh^{3+}$ on the dropping mercury ctrode in acid medium is characterised by a arp peak in the $dE/dt = f(E)$ oscillographic curves. ncn. of 0·02% of Rh in platinum and 0·005% of n in palladium and gold can be detected. The ight of the peak corresponds to the concn. of Rh the range of 0·5 μg to 25 μg in 20 ml of the ctrolyte and can be used for quant. purposes. calibration curve or the method of standard ditions can be used for the evaluation of the sults. *Procedure*—To the soln. of the sample ntaining 0·006 to 0·12 mg of Rh add *N* HCl ml) and 4 *N* NaCl (3 ml), polarograph, and measure the height of the peak. A ration of Rh to Pt or Pd of 1:2000 and Rh to Au of 1:3300 has been determined with an accuracy of $\simeq \pm 5\%$.
J. Zýka

3536. **Fire assay for platinum and palladium in ores and concentrates.** M. E. V. Plummer, C. L. Lewis and F. E. Beamish (Div. of Anal. Res., Univ. of Toronto, Canada). *Anal. Chem.*, 1959, **31** (2), 254–258.—A new method is proposed for the recovery, separation and determination of Pt and Pd. A fire-assay fusion of the sample with $Na_2CO_3$ in a carbon crucible at 1450° yields an Fe - Ni - Cu alloy button, which contains the Pt and Pd present in the original sample. A sulphide phase (matte) and a slag are also formed, the matte containing only minor amounts of Pt and Pd and the slag none. The button is dissolved in HCl, and Pt and Pd are isolated by means of a cation-exchange resin; Pt and Pd are then separated by paper chromatography and, after extraction from the chromatogram, determined spectrophotometrically. The results compare favourably with those obtained by the classical fire-assay procedure.
F. L. Selfe

3537. **New approach to the analysis of brass, cadmium and zinc plating solutions, using ethylene-diaminetetra-acetic acid and Fast Sulphon black F.** K. E. Langford. *Electroplating*, 1958, **11** (12), 439–441.—A rapid, accurate volumetric method is described. An aliquot (2 ml) of the plating soln. is evaporated to dryness in a 500-ml flask with 5 ml of conc. HCl and 5 ml of $H_2O_2$ (20 vol.). While the residue is still hot, 50 ml of $H_2O$ and 20 ml of conc. aq. $NH_3$ are added and the mixture is filtered to remove Fe. Standard copper soln. (8 g of $CuCl_2.6H_2O$ per litre) (2 ml) is added (except for brass soln.) and the soln. is diluted to 400 ml; 6 to 8 drops of 1% Fast Sulphon black F (C.I. Acid Black 32) indicator are added and the soln. is titrated with 0·2 *N* EDTA (disodium salt) to a dull green end-point.
C. H. Cowper-Coles

3538. **Quantitative X-ray determination of anatase and rutile in mixtures.** J. Wańková (Res. Inst. Inorg. Chem., Ústí nad Labem). *Chem. Průmysl*, 1958, **8** (11), 577–580.—A selective method for the determination of the content of anatase and rutile in titanium white has been developed.
J. Zýka

3539. **Methods of testing refractory materials. Additional methods.** British Standards Institution (2 Park Street, London). Addendum No. 2 (1959) to B.S. 1902:1952. 8 pp.—Additional methods are specified for the determination of silica, size of refractory bricks and shapes, bulk density and warpage (convexity and concavity).
H. M.

3540. **A rapid method for the analysis of clinker and Portland cement.** G. N. Babachev. *Zhur. Anal., Khim.*, 1958, **13** (6), 716–718.—A rapid method is described for the determination of Si, Fe, Al, Ti, Ca, Mg, $SO_4^{2-}$, $CaSO_4$ and free CaO. Silica is separated and determined by the gelatin method; Al, after pptn. with aq. $NH_3$, as the fluoride; Fe, Ti, Ca and Mg complexometrically; $SO_4^{2-}$ by igniting the sample at 1200° to 1300° and titrating the $SO_2$ liberated with iodine; $CaSO_4$ by passage of an aqueous extract of the sample through an ion-exchange column and titration of the eluate with NaOH soln., and free CaO complexometrically.
W. Roubo

3541. **Identification of glass fragments by their physical properties.** J. Finch and P. P. Williams (Dominion Lab., D.S.I.R., Wellington, New Zealand). *Analyst*, 1958, **83**, 698–699.—Measurements have been made of the physical properties of glass fragments from 61 different objects, *viz*, bottles of various types, headlamp glasses, ophthalmic lenses and window plate-glass, all of which are often encountered in forensic work. Fluorescence was observed only with ophthalmic lenses. Among 100 ophthalmic lens blanks (including some bifocals), only one did not exhibit some fluorescence. In general, different colours were observed at the two exciting wavelengths (253·6 m$\mu$ and 300 to 400 m$\mu$), and without exception the two parts of bifocals showed different fluorescence. Dispersion measurements had little significance. Ophthalmic lenses have a higher refractive index (1·5230 to 1·5242) than other glasses, but cannot be readily distinguished from one another. Bottles also tended to form a group, the range for 31 types of bottle being 1·5120 to 1·5170. Densities of ophthalmic lenses had a short range (2·5084 to 2·5184), but those of other types of object showed wide ranges, and wide ranges were found also with fragments from the same bottle. A. O. Jones

*See also Abstracts*—**3371**, Use of 2-(1-ethylpropyl)-8-hydroxyquinoline. **3372**, Colorimetric determination of Co, Pb and U. **3373**, Scheme of qual. analysis. **3376**, A new metal indicator. **3380**, EDTA titrations without metal indicators. **3381**, Indicators in complexometric titrations. **3382**, Use of tetraethylenepentamine for titration of metals. **3839**, Spectral analysis. **3846**, Determination of gases in metals. **3850**, Drop-scale chronopotentiometry. **3853**, Analysis of mixed $\gamma$-emitters.

## 3.—ORGANIC ANALYSIS

*Determination of elements and radicals and of organic compounds not included in other sections. Organic industrial products, including petroleum and its products, fuels, detergents, volatile oils, cosmetics, dyestuffs, fibres, plastics, resins, paints, elastomers, leather, explosives.*

3542. **Paper chromatography of organic substances. II. Preparative micro-methods in paper chromatography.** V. Prey, A. Kabil and H. Berbalk (Inst. f. organ. Chem., Tech. Hochsch., Vienna). *Mikrochim. Acta*, 1959, (1), 68–78.—A micro-autoclave is described suitable for the preparation of derivatives of 100 to 500 $\mu$g of organic substances. The sample is transferred to glass-fibre 'paper' and the derivative is prepared and subsequently eluted in a special apparatus (described) and identified by normal paper chromatography. Details are given for the identification of alkyl halides as pyridine derivatives; of tertiary amines as methylammonium compounds; of hydrocarbons and aromatic halides as nitro derivatives; of primary and secondary alcohols as xanthates; and of carboxylic acids as hydroxamic acids. Results are quoted for 26 compounds.

**III. Qualitative organic analysis by means of paper chromatography.** V. Prey and A. Kabil. *Ibid.*, 1959, (1), 79–86.—The scheme described is suitable for the examination of 100 to 500 $\mu$g of organic mixtures; it is based on the separation of the several constituents into groups by simpl chemical and chromatographic means, and th subsequent resolution of these groups by th methods described above. T. R. Andrew

3543. **Quantitative organic micro-analysis belo the milligram scale.** W. J. Kirsten (Inst. of Me Chem., Univ. Uppsala, Sweden). *Microchem. J* 1958, **2** (2), 179–204.—Despite improvements i instrumentation in recent times, considerab difficulties in applying the new measuring metho to a simple 'scaling down' of the Pregl combustio procedures were encountered. For decimilligra and ultramicro analysis it has generally bee necessary to design new methods for the destructio of samples and for the separation of element Available procedures are reviewed and in man cases commented on as a result of the author practical experience. Suggestions for futu workers and instrument manufacturers are offere (121 references.) D. F. Phillips

3544. **Elementary analysis using radiation source** J. S. Wiberley (Socony Mobil Oil Company Inc Brooklyn, N.Y., U.S.A.). *Microchem. J.*, 1958, (2), 219–227.—The replacement of combustio methods for C, H, O, N, Cl and S by radiatio methods within ten years is predicted. A simp method depending on the absorption of X-ra from $^{55}$Fe (half-life $\simeq$3 yr.) in petroleum sampl is described. A limitation is that the content of must be known to within 2% if S is to be correct 0·1%. Beta-rays from $^{90}$Sr may be applied to th determination of H. The moderation of fa neutrons produced by Ra - Be sources is suggeste as a means of determining H, the principle alread being used in commercially available instrumen for the measurement of H present as $H_2O$ in soil Neutron-activation techniques coupled with the us of $\gamma$-ray spectrometers offer possibilities of simu taneous determination of several elements i organic compounds. It is suggested that the bac scatter of $\beta$-rays might assist the identification of a organic compound by comparing the percentag back-scatter of the sample with the calculated bac scatters of several possible formulae.

D. F. Phillips

3545. **Determination of carbon and hydrogen i organic compounds containing phosphorus an sulphur. A rapid semi-micro method using silv permanganate.** I. Lysyj and J. E. Zarembo (Chem. Div., Food Machinery and Chemic Corp., Princeton, N.J., U.S.A.). *Microchem. J* 1958, **2** (2), 245–252.—The Körbl method (*Ana Abstr.*, 1956, **3**, 733, 1384, 3067; 1957, **4**, 909, 910 in which the conversion of C into $CO_2$ and H in $H_2O$ is accelerated by passing the products of com bustion over thermally decomposed silver pe manganate, is modified to provide good accurac and precision in the analysis of organophosphor and sulphur compounds. The silver permangana packing is used without the asbestos buffer zon A blast burner is used to heat the sample vigorous for 5 min. to effect complete combustion of pho phorus compounds. Oxides of S and P combi directly with silver wool and the central mass decomposed silver permanganate. The speci Körbl heating element used to prevent condensatio of water in the capillary end of the anhydron absorption tube is replaced by a simple steel hoo which is connected to the stationary burner.

D. F. Phillips

546. **Organic micro-analysis. XVI. An investigation on the reaction product in a modified combustion tube for direct determination of oxygen.** uo Imaeda (Pharm. Inst., Med. Fac., Kyoto v., Sakyo-ku, Kyoto). *J. Pharm. Soc. Japan*, 8, **78** (1), 30–35.—The modified combustion e containing $I_2O_5$ at the end (Kono, *J. Agric. m. Soc. Japan*, 1954, **28**, 581) and fitted with an orber containing $MnO_2$ and $Na_2S_2O_3.5H_2O$ zumi *et al.*, *J. Pharm. Soc. Japan*, 1956, **76**, 1) is suitable for the analysis of acidic compnds containing halogen and S, but gives high ılts with compounds containing N. This is to the formation of HCN, which produces and $H_2O$ on oxidation with $I_2O_5$. Attempts at fractional combustion of CO and HCN were uccessful.

**VII. An improved method of determination of bon monoxide by the Schütze method.** Kazuo ıeda. *Ibid.*, 1958, **78** (4), 386–391.—Instead of $S_2O_3.5H_2O$ for the absorption of iodine, silver rder, made by the following method, can be d—$AgNO_3$ (25 g in 500 ml of water) is treated ı NaOH (6 g in 100 ml of water), the ppt. is hed with water (500 ml), dried at 150°, then ted at 500°, and the resulting silver is washed ı 0·5% $HNO_3$ (100 ml) and water and dried 50°. The CO is passed through a triple-walled nder containing, in the middle compartment, a er layer of ≃5 g of $I_2O_5$ and an upper layer of g of the Ag; the cylinder is heated from inside central compartment by nichrome wire. The ture of iodine by the silver is quant. at 150°. outlet gas ($CO_2$) is absorbed and weighed in usual manner. This vertical cylinder can be ıched to the combustion tube for the determina- ı of N or of C and H. K. Saito

547. **Determination of nitrogen in certain rinated compounds.** T. R. F. W. Fennell and R. Webb (Royal Aircraft Estab., Farnborough, nts, England). *Analyst*, 1958, **83**, 694–695.— almost complete absence of reference to the ldahl method in published methods for the ermination of N in fluorinated compounds may e the impression that it cannot be used. A iety of solid fluorinated compounds have been cessfully analysed by the Kjeldahl method. procedure of Belcher and Godbert ("Semiro Quantitative Organic Analysis", 2nd Ed., gmans, Green & Co. Ltd., London, 1954, p. 102) used, but standard HCl was used instead of $BO_3$ to receive the distillate. Examples show no interference is caused by the presence of F, ı in compounds containing nitro groups which e subjected to reduction with P and HI before stion (Belcher and Godbert, *loc. cit.*).

A. O. Jones

548. **Determination of phosphorus in organic pounds via flask combustion.** L. E. Cohen and W. Czech (Food Machinery and Chem. Corp., tvaco Mineral Prod. Div., Carteret, N.J., A.). *Chemist Analyst*, 1958, **47** (4), 86–87.— gh solids (≯2 mg of P) on to a holder of ashless r-paper or liquids (≯15 mg of sample) into a tin capsule which is wrapped in paper. Transthe wrapped sample to the wire cage of a comion flask containing 40 ml of *N* $H_2SO_4$. Flush flask with O for 3 min. (5 min. with capsule), ignite the paper tail of the wrapped sample, t the stopper carrying the cage into the flask, slowly invert it, shaking for 2 to 3 min. after bustion is complete. Make the contents of the flask up to 500 ml. Treat an aliquot (10 ml) with 8 *N* $H_2SO_4$ (8 ml) and water (22 ml) and boil slowly for 40 min. Cool, and dilute to 40 ml with water. Add 10% ammonium molybdate soln. (8 ml) and 50 ml of solvent mixture (equal vol. of *iso*butyl alcohol and thiophen-free benzene), and shake vigorously for 20 sec. Transfer 25 ml of the solvent layer to a 50-ml flask, add 15 ml of methanolic $H_2SO_4$ (20 ml of conc. acid diluted to 1 litre with methanol) and 1 ml of $SnCl_2$ soln. (0·2 g of $SnCl_2.H_2O$ in 0·5 ml of conc. HCl and 100 ml of *N* $H_2SO_4$; fresh daily). Mix, dilute to volume with methanolic $H_2SO_4$, set aside for 10 min., then read the colour in a 20-mm cell at 625 mμ, with a slit width of 0·065 mm, against a blank prepared with a filter-paper sample holder or wrapped gelatin capsule. Refer results to a calibration curve obtained with $KH_2PO_4$ soln. (5 μg of $P_2O_5$ per ml). Five analyses of tri-*p*-tolyl phosphate gave a mean of 8·32 ± 0·077% of P, the supplier's value being 8·34%. Analyses of 7 organic phosphorus compounds showed good agreement with the calculated value or that given by the supplier. Analyses should be completed soon after the combustion, as $P_2O_5$ may be lost from the soln. (about 5% in 24 hr.) probably owing to adsorption by the glass. R. E. Essery

3549. **Analytical procedure for compounds containing boron, carbon and hydrogen.** H. Allen, jun., and S. Tannenbaum (Lewis Res. Center, Cleveland, Ohio, U.S.A.). *Anal. Chem.*, 1959, **31** (2), 265–268.—The organoboron compound is quant. oxidised with oxygen in an Inconel bomb at high temp. and pressure. The combustion products ($CO_2$, $H_2O$ and hydrated boric oxide) are separated by conventional techniques and determined. The method was successfully applied to several trialkyl-borates and -boranes. For the C, H and B determinations, respectively, the precisions are ±0·11, ±0·07, and ±0·07% absolute, and the accuracies ±0·22, ±0·12 and ±0·1% absolute, in the ranges 60 to 88%, 11 to 16%, and 3 to 11% (approx. 30 analyses). G. P. Cook

3550. **Spectrophotometric studies for the synthesis of organostibonic acids. II. Colorimetric microdetermination of antimony in organic antimony compounds.** Yahyoe Kinoshita (Pharm. School, City Univ., Mizuho-ku, Nagoya). *J. Pharm. Soc. Japan*, 1958, **78** (4), 315–319.—Experimental conditions for the colorimetric determination of Sb with rhodamine B (C.I. Basic Violet 10) (**I**) were examined with reference to the application to the analysis of organostibonic acids. The decomposition of the sample is best effected by the use of conc. $H_2SO_4$ (2 ml) and $K_2SO_4$ (0·2 g) (for ≃3 mg of Sb) followed by the addition of $H_2O_2$ (30%, 2 drops). For the extraction of Sb with di*iso*propyl ether, 6 *N* HCl is the optimum acid concn. in the presence of 0·02% of **I** (in *N* HCl, 2 ml).

K. Saito

3551. **Review of methods employed for the detection, characterisation and assay of substances having a hydroxyl group (aliphatic, aromatic and heterocyclic).** S. Veibel (Univ., Copenhagen). *Parfum. Cosmét. Savons*, 1959, **2** (1), 2–8.—In this comprehensive review, the direct methods discussed include acetylation and bromimetric determination, and indirect methods include the preparation of xanthates, S-alkylthiuronium picrates, aryloxyacetates, *m*-nitrophenylcarbamates, *p*-nitrobenzoates and 3:5-dinitrobenzoates. H. B. Heath

3552. **Semi-micro determination of the carbonyl group. Determination of phenylhydrazine and hydroxylamine.** B. Buděšínský (Res. Inst. Pharm. and Biochem., Prague). *Chem. Listy*, 1958, **52** (12), 2292–2295.—The reactions—

(*i*) $C_6H_5NH{\cdot}NH_2 + 2Cu^{2+} + 2OH^- = 2Cu^+ + C_6H_6 + N_2 + 2H_2O$,

and (*ii*) $2NH_2OH + 4Cu^{2+} + 4OH^- = N_2O + 4Cu^+ + 5H_2O$

have been applied to the potentiometric determination of phenylhydrazine (**I**) and hydroxylamine (**II**) with a pyridine - ethanolic soln. of Cu acetate, and to the indirect determination of the carbonyl group. The titration of 7 to 42 mg of **I** and 3·5 to 17·5 mg of **II** is carried out in a medium of 5 ml of pyridine with 1 ml of 0·05 *M* Cu acetate [dissolve 11 g of Cu acetate in 900 ml of ethanol - pyridine (1:1), set aside for 3 days, filter and determine the factor complexometrically or by titration of pure **I** hydrochloride; the factor changes after 3 days]. The average error is ±0·11% for **I** and ±0·46% for **II**. 2:4-Dinitrophenylhydrazine can also be determined by this method. *Procedure for carbonyl groups*—Dissolve 0·15 to 0·20 milli-equiv. of the sample in pyridine and add 38 to 40 mg of **I** hydrochloride. Remove air from the reaction mixture with a stream of N, close the flask and heat on a water bath for 15 min.; cool and titrate potentiometrically in a stream of N with 0·05 *M* Cu acetate. The suitability of the procedure has been tested with good results by the determination of the carbonyl group in acetone, ethyl methyl ketone, methyl propyl ketone, benzaldehyde, isatin, and ethyl phenylglyoxylate. J. Zýka

3553. **Determination of carbonyl compounds.** J. S. Fritz, S. S. Yamamura and E. C. Bradford (Iowa State Coll., Ames, U.S.A.). *Anal. Chem.*, 1959, **31** (2), 260–263.—The compound is oximated in methanol - *iso*propyl alcohol and the excess of hydroxylamine is titrated with standard $HClO_4$ to a potentiometric or visual end-point, with Martius yellow (C.I. Acid Yellow 24) as indicator. Recoveries from 4 compounds of known purity were >99%. The assay of 15 compounds gave results generally >98%, with an average deviation from the mean of ±0·2%. G. P. Cook

3554. **Determination of the carbamoyl grouping in non-aqueous medium.** O. Cerri, A. Spialtini and U. Gallo (Ist. Sieroterapico Milanese "S. Belfanti," Milan, Italy). *Pharm. Acta Helv.*, 1959, **34** (1), 13–18 (in French).—The method is applicable to carbamates in which there is no N-substitution. Amides, urea, thiourea, semicarbazones and biuret cause no interference. *Procedure*—Dissolve the sample (1 or 2 milli-equiv.) in pyridine (10 ml) and heat under reflux with a 0·1 *N* soln. of Na methoxide in benzene - methanol (17:3) (25 ml) for 1 hr. with exclusion of moisture. Cool and titrate with a 0·1 *N* soln. of benzoic acid in benzene, with thymol blue as indicator. Perform a blank titration. Alternatively, weigh the sodium cyanate which is pptd. during the ebullition with alkali.
A. R. Rogers

3555. **Organic micro-analysis. III. Micro-determination of the methoxyl group.** Minoru Fukuda and Tatsuei Sai (Pharm. Fac., Osaka Univ., Hotarugaike, Toyonaka). *J. Pharm. Soc. Japan*, 1958, **78** (1), 101–102.—In place of N or $CO_2$, air can be used in the distillation of alkyl iodide, following the decomposition of the methoxyl or ethoxyl gro (*e.g.*, Neuman's procedure, *Ber.*, 1937, **70**, 73 Iodine is not distilled.

**IV. A new micro-determination of methoxyl a ethoxyl groups by a combustion method.** Min Fukuda and Tatsuei Sai. *Ibid.*, 1958, **78** (1), 83– —The vapour of the distillate obtained by above-mentioned procedure is introduced, via air-cooled reflux condenser, into a combustion tu containing a platinum catalyst, and the liberat iodine is absorbed by rolled silver gauze for sub quent gravimetric determination. Iodine is insta taneously captured at >150° (30 minutes' flow, a rate of <20 ml per min.). The sample (3 mg) dissolved in a mixture of phenol and propio acid (4:1, by wt.) (0·5 ml) and boiled with (sp. gr. 1·7, previously distilled over red phosphor (2 ml) in a current of air (10 ml per min.) for 30 m
K. Saito

3556. **Gas-chromatographic micro-determinati of formyl and acetyl groups, particularly in digita glycosides.** H. Spingler and F. Markert (Forschun lab. der Fa. C. F. Boehringer u. Söhne, Mannhei Waldhof). *Mikrochim. Acta*, 1959, (1), 122–128. A sample (0·005 to 0·02 milli-equiv.) is heated w 20 mg of toluene-*p*-sulphonic acid and 300 µl methanol for 30 min. in an oil bath at 70° to 8 The distillate is collected in a graduated receiv cooled to −10° by an ice - salt mixture. The v of distillate is recorded and a 20-µl aliquot transferred to a Perkin-Elmer 'Fractometer' 154 Gas chromatography is carried out, with helium carrier gas. Good results are reported for substances (errors −0·95% to +0·45% absolut
T. R. Andrew

3557. **Experiments in the analysis of the ac functional group. Conclusion.** E. A. M. F. Dahm (Koninklijke/Shell Lab. Amsterdam, Holland *Chim. Anal.*, 1958, **40** (11), 430–434.—A review suitable methods of determining carboxylic acids concluded. The determination of formic acid, the presence of acetic acid, by oxidation wi Pb tetra-acetate, and analysis by azeotropic distill tion with $CHCl_3$ are discussed. For small quantiti of acetic acid in the presence of formic acid the ma spectrometer is preferred, and the distribution intensities in the various mass peaks for 9 acids given. For several acids, gas chromatography the preferred method and is described.
E. J. H. Birch

3558. **Titanous chloride as a reagent for quan tative organic micro-analysis. I. Micro-determin tion of nitro and nitroso groups.** T. S. Ma and J. Earley (Dept. of Chem., Brooklyn Coll., N.Y U.S.A.). *Mikrochim. Acta*, 1959, (1), 129–140 ( English).—Titanous chloride soln. (0·04 *N*) h been stabilised by adding 100 ml of 12 *N* HCl a 200 g of amalgamated zinc per litre and preventi photo-oxidation by wrapping the storage ves with aluminium foil. To determine nitro co pounds, weigh 3 to 8 mg into a modified Erlenmey flask (illustrated) containing 4 ml of ethanol (95% stir until dissolved, attach to a modified Machl micro-burette, add 7 ml of 2·5 *M* Na acetate a flush with N at 20 ml per min. for 5 min. Titra with 0·04 *N* $TiCl_3$ until the soln. is deep violet a set aside for 3 min. Add 4 ml of 12 *N* HCl a connect to a 5-ml micro-burette. Titrate wi 0·035 *N* $(NH_4)_2SO_4.Fe_2(SO_4)_3$ until the blue colo is almost discharged, add 2 ml of 2·5 *M* $NH_4S($ and continue the titration until a pink colo

ble for 1 min., is obtained. The procedure is odified slightly for nitroso compounds: 4 to 9 mg dissolved in 5 to 10 ml of water or ethanol, nl of 2·5 *M* Na acetate is added, and 0·03 *N* $TiCl_3$ d 0·025 *N* $(NH_4)_2SO_4.Fe_2(SO_4)_3$ used for titration. Nitroso compounds must be allowed to stand for min. with a 50 to 150% excess of $TiCl_3$ before ding HCl. Nineteen nitro and 10 nitroso mpounds have been studied and good results ±0·5% relative error) reported, except for aliphatic tro compounds and aromatic compounds having e nitro group in a side-chain. Cupferron gave gh results owing to cleavage of the N–N bond. Nitroso compounds (not N-nitroso) may be termined in the presence of some nitro compounds replacing the Na acetate soln. by 12 *N* HCl.

T. R. Andrew

3559. **Identification and determination of O- and benzylidene groups.** M. Jureček and K. Obruba nst. Anal. Chem., High-School of Chem. Technol., rdubice, Czechoslovakia). *Chem. Listy*, 1958, (11), 2066–2072.—The semi-micro- and micro-ethod described is based on the fission of the nzylidene groups by acid hydrolysis, and distillaon of the benzaldehyde so produced into a known cess of 4-nitrophenylhydrazine (**I**) or 2:4-dinitrohenylhydrazine (**II**) soln., the excess of which, ter the separation of the hydrazone, can be termined volumetrically with $Ti^{3+}$. *Procedure*—ace the sample (10 to 15 mg if using **II**; 20 to 25 g if using **I**; 4 to 6 mg for the micro-determination th **II**) into a distillation apparatus modified cording to Kuhn and Roth (*Ber.*, 1933, **66**, 1274), d $H_2SO_4$ (60%) (5 ml), heat for 30 to 40 min. at 5° to 140°, distil the benzaldehyde with $H_2O$ to an absorption vessel containing 0·01 *M* **II** 0 ml) or 0·02 *M* **I** (10 ml). Set aside for 1 hr. ith **II**) or 6 to 8 hr. (with **I**). Filter off the ppt. d wash 5 to 6 times with 2 *N* HCl (30 ml with **II**, ml with **I**, or 10 ml in the micro-determination); ld to the filtrate 2 ml of a mixture of conc. HCl d 40% HF (13:1), remove O by bubbling for 5 in. with N, add 0·4 *N* $TiCl_3$, boil for 30 min. in atmosphere of N, cool, add $NH_4SCN$ soln. as dicator and titrate with 0·1 *N* $(NH_4)_2SO_4.Fe_2(SO_4)_3$ l pink. Benzylidene diacetate, tribenzylidene annitol, benzylidine-*o*-aminophenol, benzylidene-nitroaniline, dibenzylidenebenzidine, dibenzylidene-*p*-phenylenediamine, benzaldehyde 2:4-nitrophenylhydrazone and benzaldehyde semirbazone have been determined by this procedure, d good results were obtained. **II** is preferred as agent on account of the lower solubility of the drazone.

J. Zýka

3560. **Rapid photometric determination of phosphine in acetylene.** Fumikazu Kawamura and roshi Namiki (Fac. of Engng, Yokohama Univ., nami-ku). *Japan Analyst*, 1958, **7** (11), 691–695. The absorption of $PH_3$ in 0·3% aq. bromine soln. oceeds rapidly; the excess of Br is reduced with $_2SO_3$, and neither $Br^-$ nor $Na_2SO_3$ interferes with e colorimetric determination of P by the molybnum blue method. The amount of $PH_3$ in etylene differs appreciably according to the nditions under which $CaC_2$ reacts. The time cen for an analysis is 15 min. *Procedure*—llect the sample (50 ml) in a syringe and inject gas into 0·3% aq. bromine soln. (20 ml) within min. Add $Na_2SO_3$ soln. (10%) until the soln. comes colourless. Dilute the product to 50 ml er the addition of ammonium molybdate soln. (1·5% in 6·5 *N* $H_2SO_4$) (5 ml) and $SnCl_2$ (2% in *N* HCl) (0·25 ml), set aside at 25° for 10 min. and determine the P colorimetrically.

K. Saito

3561. **Determination of 1:2-dibromoethane in brine.** J. R. Marshall and D. A. Ader (Israel Mining Ind. Lab., Haifa). *Analyst*, 1958, **83**, 687–688.—The method was developed for the determination of 1:2-dibromoethane (**I**) in brine obtained during the manufacture of **I**. The brine, containing 10 to 200 mg of **I**, is extracted three times with xylene (4 to 5 ml). The separated extract is washed free from $Cl^-$ and is then heated under reflux with KOH (4 to 5 g) and *n*-butanol (a solvent for KOH and xylene) in a bath of saturated NaCl soln. for 1 hr. The digest is diluted, neutralised with dil. $HNO_3$, slightly acidified with the same acid, and $Br^-$ are pptd. as AgBr. The collected ppt. is washed with water to remove $AgNO_3$ and with *iso*propyl alcohol to remove xylene, dried at 120° to 130°, and weighed, and the weight is corrected for a reagent blank. If the brine sample contains free halogen, this is converted into halide by addition of excess of KI and titration of the liberated iodine with $Na_2S_2O_3$ soln. before extraction of the sample with xylene. Quoted results with samples of known **I** content indicate an accuracy within ±1%.

A. O. Jones

3562. **Determination of alcohols by oxidation.** P. Jaulmes and R. Mestres (Fac. de Pharm., Montpellier, France). *Chim. Anal.*, 1958, **40** (11), 413–424.—After a review of oxidative methods of determining alcohols, a standard procedure is described, based on the method of Semichon and Flanzy (*Ann. Falsif.*, 1929, **139**, 414). The oxidising soln. is 0·276 *N* with respect to $K_2Cr_2O_7$ and 7 *N* with respect to $H_2SO_4$ (20% v/v). After various times of oxidation the excess of $K_2Cr_2O_7$ is determined by titration with $Fe^{2+}$, with ferrous 1:10-phenanthroline as indicator, correcting any slight excess at the end-point by back-titrating with $KMnO_4$ soln. Volatile acids formed are determined after steam-distillation. Ethanol can be quant. determined, since oxidation to acetic acid is complete in 30 min. and the acetic acid is not attacked except under more drastic conditions. It is suggested that this chemical method could be used to standardise the various tables of 'alcoholic degrees' which vary from country to country. With methanol, the formic acid produced is oxidised under the standard conditions and the only possible method of analysis is to oxidise completely to $CO_2$ and $H_2O$, requiring 12 hr. A mixture of methanol and ethanol may be determined by a 12-hr. oxidation (total alcohol) followed by determination of the volatile acid produced (acetic acid from the ethanol only). Oxidations of higher primary alcohols are described under the standard conditions and more and less rigorous ones, and in all cases acids with fewer C atoms than the alcohol are produced in addition to the expected acid. Under the standard conditions these alcohols consume 2·45 to 2·8 (usually 2·75) atoms of O per mol. in 24 hr. The nature of the alcohol can be qual. determined by paper chromatography of the acids liberated. *iso*Propyl alcohol is oxidised quant. to acetone in 15 min. by the standard oxidant, and the acetone is not oxidised in 8 days. (With 47·7% $H_2SO_4$ the acetone is oxidised in 4 days to acetic acid which is itself considerably oxidised.) *sec.*-Butyl alcohol is oxidised slowly but quant. to acetic acid (3 atoms of O per mol. in 3 months). Oxidation of tertiary alcohols is very slow. Allyl alcohol is quant.

oxidised very rapidly, consuming 8 atoms of O per mol. and forming $CO_2$ and $H_2O$. Benzyl alcohol is quant. oxidised in 5 to 6 hr. to benzoic acid, which remains unoxidised under the standard conditions for 8 days. Lactic acid consumes 2 atoms of O per mol. in 4 hr. and is not further oxidised in 16 months. E. J. H. Birch

3563. **Chromatography of alcohols and phenols. Methods of isolation and characterisation of alcohols.** B. Gastambide. *Parfum. Cosmét. Savons*, 1958, **1** (11), 423–427.—Conditions influencing the adsorption of the hydroxyl group in partition chromatography are discussed. Methods of obtaining primary and secondary alcohols in an aqueous phase are reviewed. The preparation of malonates by reaction with malonyl chloride is described, the melting-points of the derivatives being used as a means of identification. H. B. Heath

3564. **Determination of *tert.*-butyl alcohol and acetone concentrations in the products of *iso*butane oxidation by infra-red absorption spectra.** G. B. Meluzova and A. A. Babaeva (M.V. Lomonosov Moscow State Univ.). *Zhur. Anal. Khim.*, 1958, **13** (6), 706–708.—A trap, immersed in liquid nitrogen, is used to freeze the gaseous products of the reaction. Exactly 2 ml of $CCl_4$ as solvent is introduced into the trap and measurements are carried out at 1718 and 918 $cm^{-1}$. The extinction coefficient $K$ for 1718 $cm^{-1}$ for acetone is 300 $mol^{-1}$ l/$cm^{-1}$ at the spectral width of the slit of 12 $cm^{-1}$ and this coefficient for 918 $cm^{-1}$ for *tert.*-butyl alcohol is $K = 90$ $mol^{-1}$ l/$cm^{-1}$ at the spectral width of the slit of 6 $cm^{-1}$. Apparatus corrections are not required. Results are accurate to within ±3%. W. Roubo

3565. **Micro-determination of glycerol in *Acetobacter* culture media.** C. P. Jackson and K. Ramamurti (Chem. Dept., Div. of Ind. Biochem., Manchester Coll. of Sci. and Technol., England). *J. Sci. Food Agric.*, 1958, **9** (12), 787–791.—Metabolites from glycerol attacked by *Acetobacter acetigenum* are destroyed by oxidation with $Ce(SO_4)_2$ and hypoiodite and the residual glycerol is determined colorimetrically. *Procedure*—Heat a 2-ml sample (0·1 to 0·5 mg of glycerol) with 1·2 ml of 10 *N* $H_2SO_4$ and 2 ml of 0·01 *N* $Ce(SO_4)_2$ at 100° for 5 min.; precipitate the excess of $Ce^{4+}$ with NaOH and centrifuge. Decant the supernatant liquid, wash the residue twice and combine the supernatant liquids (total vol. 20 ml). Add 4 drops of 0·1 *N* iodine, set aside in darkness for 10 min. and add 2 ml of 10 *N* $H_2SO_4$. Add 5 ml of 0·1 *M* $HIO_4$ and, 5 min. later, 5 ml of *M* $Na_2AsO_3$; 10 min. after decolorisation of the iodine, dilute to 100 ml and treat 1 ml with 10 ml of 0·2% chromotropic acid in 10 *N* $H_2SO_4$ at 100° for 30 min. Cool and measure the extinction at 580 mμ; 0·1 to 0·5 mg of glycerol can be determined in the presence of 0·76 mg of dihydroxyacetone. The precision is related to the accuracy of prediction of the amounts of glycerol in unknown soln. from standard curves prepared with aq. glycerol soln.; 95% confidence limits over the determinative range from 0·1 to 0·5 mg of glycerol are ±0·01 mg to ±0·011 mg. The limitations of the method are discussed. P. D. Parr-Richard

3566. **Paper-chromatographic analysis of carbohydrates.** F. Schneider and A. Emmerich (Inst. f. Landwirtschaft. Technol. u. Zuckerindust., Tech. Hochsch., Braunschweig). *Stärke*, 1959, **11** (1), 1–7.—This concise review describes also the use of the double salt of dimethyl-*p*-phenylenediamin hydrochloride and $SnCl_2$ as a universal reagent fo the detection of reducing and non-reducing sugar and similar substances. On a pink backgroun aldoses appear as yellow-brown spots, ketose carmine, and pentoses strong red. Oligosaccharide are hydrolysed by the acid reagent and appear a a mixture of the colours given by their component The reagent is sensitive to 3 μg but can be improve to detect 1 μg by using u.v. light. The bes solvents are *n*-butanol-acetic acid-water (4:1:5 and *n*-propanol-ethyl acetate-water (7:1:2 Explanations are given of the de Bruyn-va Ekenstein transformation and the formation o oligomers arising from glucose and fructose whe heated in alkaline, acid or neutral media. E. Dux

3567. **Qualitative test for aldehyde in acetone** M. Zeman, M. Klátil and K. Pánek (Chem. Lab Svit n.p., Gottwaldov, Czechoslovakia). *Chem Průmysl*, 1958, **8** (12), 638–639.—Schiff's an Tollens' reagents have been studied for the reli ability of their use for the detection of aldehyde in commercial acetone. It is concluded that thes reagents are unsuitable for this purpose, because positive reaction has been obtained even wit chemically pure or specially purified specimens o acetone. No difference has been observed whe testing purified and technical samples of aceton by these methods. It is concluded that for suc cases the Schiff's and Tollens' reactions are un reliable and that the polarographic method i preferable. J. Zýka

3568. **Simple spot test for methyl ketones.** T. W Stanley (Taft Engng Center, U.S. Dept. of Health Education and Welfare, Cincinnati, Ohio). *Chemis Analyst*, 1958, **47** (4), 91.—Replacing $(NH_4)_2SO$ with ammonium acetate in the nitroprusside tes for acetone bodies, renders the test more sensitiv and specific than the older versions; it can b carried out in methanol soln., and is applicable t compounds insol. in water. The reagent (3 part of sodium nitroprusside, 50 parts of ammoniu acetate and 50 parts of anhyd. $Na_2CO_3$, ground to uniform powder) is satisfactory if stored in a tightl stoppered bottle and used within 24 hr. For th test, overlay 50 mg of reagent with 0·1 ml of methanolic soln. of the suspected compound, se aside for 10 to 30 min., and note the colour. Fo the determination of wavelength maximum, overla 50 mg of reagent with 1 ml of methanol containin 1 mg of compound, allow the colour to develop an examine the absorption between 525 and 640 mμ Colours (purple, blue or green), wavelengths of max absorption and detection limits (usually 1 to 5 μg are listed for 20 compounds that give a positiv reaction, and a further 12 compounds that do no respond to the test are named. R. E. Essery

3569. **Chromatography of organic compounds I. Separation of thiosemicarbazones of aliphati ketones by paper chromatography.** J. Franc (Res Inst. Org. Synth., Pardubice-Rybitví, Czecho slovakia). *Chem. Listy*, 1958, **52** (12), 2311–2315.— The chromatography was carried out by the des cending technique on Whatman paper No. 1 impregnated with a 30% ethanolic soln. of form amide or dimethylformamide, or with a 20% soln of acetamide. Aliquots (2 to 10 μg) of the thio semicarbazone dissolved in ether were placed o the paper and developed with various solven systems [$CCl_4$, chlorobenzene, chloro*cyclo*hexan

l *cyclo*hexane - *n*-butanol (25:1)] at 26° to 31°. r the detection, the chromatogram was moistened :h 5% $AgNO_3$ soln. and passed through 1 to 2% $NH_3$ soln. (black spots). As little as 1 to 2 μg a thiosemicarbazone can thus be detected; the :ection can also be made with a 1% soln. of limethylaminobenzaldehyde (**I**) in 2 *N* HCl ellow spots, blue or orange in u.v. light). Thio- nicarbazones were prepared by heating 1 ml of :one and 1 g of thiosemicarbazide (**II**) under lux on a water bath for 1 hr., cooling and extract- ; with diethyl ether. *Determination of methyl- clo*hexanone (**III**) *in technical* cyclo*hexanone*— ssolve **I** (1 g) in $H_2O$ (25 ml) with heating, add the mple (1 ml) dissolved in ethanol (2 to 3 ml) and at for 5 to 10 min. Filter off the crystals on a ss filter (G3), wash with $H_2O$, dissolve in ethanol d separate chromatographically on Whatman per impregnated with 25% formamide soln., th *cyclo*hexane - *n*-butanol (25:1) as solvent. r the semi-quant. evaluation, a comparison ile (0·25 to 1% content of **III**) was prepared. *termination of* p-*tolualdehyde in technical dimethyl ephthalate*—Heat the sample (1 g) with **II** (1 g) d ethanol (3 ml) for 1 hr. under reflux. Extract th diethyl ether and evaporate to 5 ml. Treat 25 ml of the extract chromatographically as scribed above, detect the spots with **I** and compare th a soln. of a standard. $R_F$ values are given for compounds. Some theoretical relations are scussed. J. ZÝKA

3570. **Gas - liquid chromatographic analysis of me oxygenated products of cool-flame combustion.** Kyryacos, H. R. Menapace and C. E. Boord hio State Univ., Columbus, U.S.A.). *Anal. em.*, 1959, **31** (2), 222–225.—Hitherto unidenti- ble compounds recognised include ethylene ide, propionaldehyde, acetone, acraldehyde, tetra- dro-*trans*- and -*cis*-2:5-dimethylfuran, *n*-butyr- dehyde, ethyl methyl ketone, methyl vinyl ketone, ethyltetrahydrofuran, methanol and croton- dehyde. Identification was assisted by means of . spectrophotometry. G. P. COOK

3571. **Paper chromatography of saturated ali- atic monocarboxylic acids.** F. Baykut and S. aykut. *Rev. Fac. Sci. Univ. İstanbul, Ser. C*22, 57, 267–270 (in German).—A simple mathe- atical relationship was worked out between the $R_F$ value and the number of C atoms in the homo- gous series of higher aliphatic saturated mono- rboxylic acids from $C_{10}$ to $C_{22}$. Light petroleum oiling-range 190° to 200°) was used as the station- y phase, and light petroleum saturated with a % acetic acid - water mixture as the mobile ase. Strips of special paper (40 cm × 14 cm) ere hung from a balance under a hood. Light troleum was first injected on to the paper and the tty acid, in $CHCl_3$ soln., was applied at the starting int. The paper was allowed to stand for 24 hr. 25° ± 0·1°. The mobile phase was then applied d allowed to act for 8 to 20 hr. The papers were ied at 110° and then placed in a Cu acetate soln. sol. copper salts of the fatty acids were formed. e excess of Cu acetate was washed away with ater containing 2 ml of acetic acid. The chrom- ogram was then dipped in 2% $K_4Fe(CN)_6$ n. for 5 min. The fatty acids were then revealed brown spots. A table is given showing the mber of C atoms of the acids and the corre- onding $R_F$ values. A graph is also plotted for is relationship. From this an equation is given, $R_F = 1{\cdot}671 - 0{\cdot}1326n + 0{\cdot}0028n^2$, where $n$ is the number of C atoms in the fatty acid.

CHEM. ABSTR.

3572. **Thermometric titration of weak monoprotic acids.** J. Jordan and W. H. Dumbaugh, jun. (Pennsylvania State Univ., University Park, Pa., U.S.A.). *Anal. Chem.*, 1959, **31** (2), 210–213.—Four acids, whose ionisation constants covered a range of 9 orders of magnitude, were studied at concn. of $10^{-3}$ to $10^{-1}$ *M*. Kinetic effects were eliminated by using an automatic procedure which maintained the rate of addition of the titrant (NaOH) to one millionth of the prevailing rates of neutralisation. The end-points were precise and accurate to ±1% for concn. $< 3 \times 10^{-3}$ *M*. Within the range studied, ionisation constants had no effect on the precision and accuracy because the heats of neutralisation were approx. equal. The experimental method was that of Jordan and Alleman (*Anal. Chem.*, 1957, **29**, 9). G. P. COOK

3573. **Control methods in lactic acid production. V. Improvement of accuracy in the determination of lactic acid.** A. Šepitka (Dept. of Carbohydrates and Biochem., Chem. Inst. Acad. Sci., Bratislava, Czechoslovakia). *Chem. Zvesti*, 1958, **12** (12), 699–702.—A method for the calculation of the purity of lactic acid from its concn. and density at 20° by means of a table of densities at various concn. of pure lactic acid is described. J. ZÝKA

3574. **Quantitative determination of glyoxylic acid.** D. N. Kramer, N. Klein and R. A. Baselice (Army Chem. Center., Md., U.S.A.). *Anal. Chem.*, 1959, **31** (2), 250–252.—The method is based on the formation of the intensely coloured 1:5-diphenylformazancarboxylic acid, obtained by the mild oxidation of glyoxylic acid phenylhydrazone in the presence of phenylhydrazine. Beer's law is obeyed at 520 mμ in the concn. range $10^{-4}$ to $10^{-6}$ *M*. The precision is ±5%. With suitable modifications the method may be used as a general procedure for aldehydes. Alcohols, ketones, acids and esters, excepting formates, do not interfere.

G. P. COOK

3575. **Spot-test detection of N-cyano compounds.** F. Feigl and V. Gentil (Lab. da Prod. Mineral, Min. da Agric., Rio de Janeiro, Brazil). *Mikrochim. Acta*, 1959, (1), 44–45 (in English).—The solid or a drop of its soln. is heated in a small test-tube with a few zinc granules and several drops of HCl (1:5). The mouth of the tube is covered with a reagent paper and the tube immersed in boiling water. A blue colour indicates the presence of an N-cyano compound. The reagent paper is prepared just before use by impregnating filter-paper with a fresh soln. made by mixing equal vol. of (*a*) 0·286% aq. $Cu^{II}$ acetate soln. and (*b*) 675 ml of satd. aq. benzidine acetate soln. diluted with 525 ml of water. Approx. 10 μg of N-cyano compound may be detected in one drop. T. R. ANDREW

3576. **Spot test for aliphatic and aromatic cyanides.** F. Feigl, V. Gentil and E. Jungreis (Lab. da Prod. Mineral, Min. da Agric., Rio de Janeiro, Brazil). *Mikrochim. Acta*, 1959, (1), 47–50 (in English).—Aliphatic and aromatic cyanides evolve HSCN when heated in the presence of sulphur. Mix the sample with 10 mg of sulphur in a micro test-tube, cover the mouth of the tube with a filter-paper impregnated with acidified $FeCl_3$ soln. (1%), and heat, starting at the upper portion of the tube and moving

downwards. A red spot is given by 1 to 20 $\mu$g of cyanides. Compounds containing C=N groups interfere and must be separated. Aliphatic cyanides give off HCN when heated in the presence of CaO and $CaCO_3$. The sample is mixed with a few mg of CaO - $CaCO_3$ mixture (1:1) in a micro test-tube, the mouth is covered with $Cu^{II}$ acetate - benzidine acetate paper, and the tube is heated in a glycerol bath at 250°. A blue stain is given by 2 to 50 $\mu$g of aliphatic cyanide. This test is specific for aliphatic cyanides. T. R. ANDREW

3577. **Polarographic determination of nitriles.** M. I. Bobrova and A. N. Matveeva-Kudasheva (Leningrad. Inzhenerno-Ekonomichesk. Inst.). *Zhur. Obshch. Khim.*, 1958, **28** (11), 2929–2932.—The work previously reported (*cf. Anal. Abstr.*, 1958, **5**, 567) is continued. The basal soln. are 0·14 *N* LiCl in 50% or 75% ethanol. Cinnamonitrile (in 75% ethanol) has a $E_{\frac{1}{2}}$ of −1·95 V; α-phenylcinnamonitrile (**I**) has a $E_{\frac{1}{2}}$ of −1·85 V (in 75% ethanol) and of −1·94 V (in 50% ethanol); fumaronitrile (**II**) (in 50% ethanol) has two waves with $E_{\frac{1}{2}}$ of −1·30 and −2·2 V; and αα′-azo*iso*-butyronitrile (**III**) (in 50% ethanol) has a $E_{\frac{1}{2}}$ of −1·80 V. In all cases the value of the limiting diffusion current is directly proportional to the concn. of the nitrile. The number of electrons transferred per molecule of nitrile are 0·48, 0·92, 0·64, 0·32 (first stage) and 0·38 (second stage), and 0·35, respectively, these fractional values indicating the irreversible nature of the polarographic reduction. When polarographing mixtures of **I**, **II** and **III**, the resulting polarograms have diffusion waves corresponding to the reduction of each component. C. D. KOPKIN

3578. **Solubility of ethylenediaminetetra-acetic acid (Complexone II) as a function of pH.** P. Mechelynck and W. Schietecatte (Section de Chim. Anal., Centre d'Étude de l'Énergie Nucléaire, Mol, Belgium). *Anal. Chim. Acta*, 1958, **19** (6), 577–579 (in French).—The solubility of EDTA in soln. of pH 1·13 to 7·3 has been determined by amperometric titration of satd. soln. with standard $Zn^{2+}$ soln. The solubility reaches a minimum of $1·73 \times 10^{-4}$ *M* at pH 2 and rises to about 2 *M* at pH 4·6 to 7·3. T. R. ANDREW

3579. **Micro-determination of maleic hydrazide by reductive cleavage with zinc in sulphuric acid.** Yasutoyo Nagai (Fac. of Agric., Tokyo Univ., Hongo). *J. Agric. Chem. Soc. Japan*, 1958, **32** (11), 851–855.—Maleic hydrazide (**I**) produces hydrazine quant. when heated with zinc in *N* $H_2SO_4$. The product is determined colorimetrically with *p*-dimethylaminobenzaldehyde (**II**) (*cf.* Wood *Anal. Abstr.*, 1954, **1**, 1125). This method is much simpler than that involving the decomposition of **I** with zinc in NaOH. Ascorbic acid and fructose interfere. *Procedure*—Heat the sample soln. (1 ml) with 8 *N* $H_2SO_4$ (1 ml) and zinc dust (300 mg) at 110° for 2 hr. Add **II** (2% in 2 *N* $H_2SO_4$, 1 ml) and water (8 ml) and measure the extinction at 300 m$\mu$ after 30 min. K. SAITO

3580. **Determination of maleic hydrazide. III. Conductimetric titration.** Shigeru Shimomura (Fac. Pharm., Tokushima Univ., Sho-machi). *J. Pharm. Soc. Japan*, 1958, **78** (6), 589–593.—The effect of impurities, including hydrazine (**I**), maleic acid (**II**) and N-aminomaleimide (**III**), upon the conductimetric titration of maleic hydrazide (**IV**) with *N* NaOH was examined. There is no interference from **I** and diethylamine (solvent for commercial products). A half-equiv. of **II** and **III** reacts with NaOH, but the slope of the graph of conductance *vs.* vol. of NaOH soln. is different from that for **IV**, two inflection points being observed for **IV** containing **II** and **III**. The amount of NaOH required to reach the first inflection point corresponds to that consumed by **II** and **III**. This amount is subtracted from the amount of NaOH consumed between the two inflection points, and the purity of **IV** calculated. To make the first inflection point sharper, the addition of a known amount of $H_2SO_4$ (0·1 *N*) is recommended. K. SAITO

3581. **Determination of dimethylurea in the presence of methylurea.** F. Jančík, B. Kakáč and V. Vaníček (Res. Inst. of Pharm. and Biochem., Prague). *Chem. Listy*, 1958, **52** (11), 2181–2183.—Methylurea (**I**) reacts with *p*-dimethylaminobenzaldehyde (**II**) to give a yellow coloration. NN′-Dimethylurea does not interfere. *Procedure*—Dissolve the sample (containing 0·2 to 0·3 mg of **I**) in a 25-ml flask in a little twice-distilled $H_2O$, add the reagent (2 g of **II** dissolved in 100 ml of 95% ethanol and 20 ml of conc. HCl) (10 ml), dilute with $H_2O$ to vol. and measure the extinction after 10 min., with violet filter No. 601 ($E_{max.}$ = 420 to 425 m$\mu$). The colour is stable for 6 hr. Refer the results to a calibration curve. Beer's law is obeyed between 0·2 and 1·6 mg of **I** in 25 ml. The average error is ±1·21%. Compounds with primary amino groups interfere. A method for the analysis of binary mixtures of **I** with NN′-dimethylurea, based on determination of the freezing-point, is also described. If wet samples are being analysed, a correction, determined by means of the Karl Fischer method, must be applied. J. ZÝKA

3582. **Ultra-violet photometric micro-determination of biuret as the manganese complex.** Yasuto Watanabe (Fac. of Agric., Kyushu Univ., Hakozaki, Fukuoka). *J. Agric. Chem. Soc. Japan*, 1958, **32** (11), 842–847.—The u.v. absorption of the complexes of biuret with various metal ions was examined and it was found that $Mn^{2+}$ gave a distinctive strong absorption at 223 m$\mu$; the extinction is proportional to the concn. of biuret for 0·1 to 1 mg per 10 ml in 0·8 *N* NaOH. In this soln. excess of $Mn^{2+}$ is pptd. as hydroxide. Biuret is separated by paper chromatography with *n*-butanol satd. with water, the spot is cut out, and immersed in an aq. soln. (10 ml) containing 2 *N* NaOH (4 ml) and $MnSO_4$ (10 mg per 100 ml) (2 ml) for 10 min., then centrifuged at 3000 r.p.m. for 10 min. The supernatant liquid is measured photometrically. K. SAITO

3583. **Reactions of amides with formaldehyde. XI. The determination of bound formaldehyde in urea - formaldehyde condensation products.** R. Květoň (Sběrné Suroviny, Střelské Hoštice, Czechoslovakia). *Chem. Listy*, 1958, **52** (11), 2178–2180.—The behaviour of urea - formaldehyde condensation products in alkaline and acid media is said to depend on the character of the substituents on the urea nitrogen. $CH_2OH$ groups in the presence of $CH_2$ and $OCH_2O$ groups can be determined iodimetrically (de Jong and de Jong, *Rec. Trav. Chim. Pays-Bas*, 1952, **71**, 643) when sol. condensates are being analysed. For insol. condensates the cyanide method is preferred (*cf.* de Jong, *Brit. Abstr. C*, 1953, 509). J. ZÝKA

584. **Scheme for the colorimetric determination microgram amounts of thiols.** B. Saville (Chem. ence Expt. Estab., Porton Down, Salisbury, ts., England). *Analyst*, 1958, **83**, 670–672.— thiol soln. (1 ml) in water or aq. ethanol is ed to 5 ml of $HNO_2$ soln. ($NaNO_2$ - dil. $H_2SO_4$) after 0·5 to 5 min., according to the nature of thiol, 1 ml of a 0·5% aq. soln. of ammonium phamate is added to remove the excess of $HNO_2$, the liquid is well shaken. The S-nitrosothiol med is hydrolysed and a diazonium salt is formed the addition of a soln. of sulphanilamide and $Cl_2$ in dil. HCl and finally a freshly prepared soln. N-1-naphthylethylenediamine dihydrochloride HCl is added. When colour development is plete the vol. is adjusted, and the colour is asured against an appropriate blank in a Spekker orptiometer with Ilford No. 605 filters. The uracy depends on the concn. of the thiol soln., ranges from ±10% for 1 ml of 0·00002 *M* thiol ±1 to 2% for 0·00004 *M* soln. Owing to the tive rapidity of the reaction, interference from all amounts of such compounds as dialkylamines negligible. As the rate of S-nitrosation of teine is much greater than the rate of de-amina- of simple amino acids, cysteine can be deter- ed without interference from large excesses of ino acids in protein hydrolysates.

A. O. Jones

585. **Colorimetric micro-determination of thiols alcoholic medium with N-ethylmaleimide.** J. ekhuysen (Service de Recherches, C.E.R.I.A., ssels, Belgium). *Anal. Chim. Acta*, 1958, **19** 542–547 (in French).—Thiols react with N- ylmaleimide (**I**) in alkaline abs. *iso*propyl hol (**II**) to give a red colour, and the necessary erimental conditions for the satisfactory quant. lication of this reaction have been studied. 0·2 ml of **I** soln. in **II** (0·5 *M*) with 1 ml of a . of the thiol in **II**. Set aside for 4 or 5 min., 1 ml of KOH soln. in **II** (0·025 *N*), mix, and 2·5 ml of **II**. Measure the extinction at 515 mμ, min. after the addition of KOH. Beer's law beyed between 0·01 and 0·10 μg of –SH and the our is stable for 15 min. T. R. Andrew

586. **Determination of alkylarylsulphonates by a-violet absorption.** R. M. Kelley, E. W. Blank, E. Thompson and R. Fine (Colgate-Palmolive , Jersey City, N.J., U.S.A.). *Bull. A.S.T.M.*, 9, (237), 70–73.—In the spectrophotometric cedure described, the strong max. extinction of il. aq. soln. (≃10 to 12 p.p.m.) of an alkylaryl- honate is measured at 224 mμ in a 1-cm quartz *vs.* a water blank. Readings do not vary with and conform to Beer's law. A quartz flow-cell ht path ≃0·03 cm) inserted in series in the mal assembly enables higher concn. (0·3 to 0·5 g litre) to be used. Interferences (mainly com- nds containing the phenyl chromophore) and ir control are discussed; the extinction of phos- tes, silicates, $CO_3^{2-}$ and carboxymethylcellulose low. The accuracy is equiv. to that of the rnative routine methods for most commercial ergents. W. J. Baker

587. **Spot tests for aromatic compounds using 4:7-trinitrofluorenone.** H. T. Gordon and M. J. raux (Univ. of California, Berkeley, U.S.A.). *al. Chem.*, 1959, **31** (2), 302–307.—Many aromatic npounds form coloured complexes when 10 μg is tted on filter-paper and sprayed with 2:4:7- itrofluorenone in benzene (0·5%). Some com- nds show brilliant u.v. fluorescence. Qualitative information of the structure of unknown compounds can be easily derived from the colour and fluorescence reactions and by determination of the solubility of the complex in *iso*octane and ethanol. The procedure is suitable for paper chromatography. Data for over 300 compounds are listed.

G. P. Cook

3588. **Rapid determination of aliphatic hydrocarbons in benzene of special reagent grade by gas chromatography.** Tsugio Takeuchi and Fukuzoo Hayakawa (Fac. of Engng, Yamanashi Univ., Motoyanagi-cho, Kofu). *Japan Analyst*, 1958, **7** (11), 712–716.—When pure benzene was submitted to gas chromatography (stationary phase, tritolyl phosphate, Carbowax or dioctyl phthalate; carrier gas, H; rate of flow, 60 ml per min.; sample, 0·1 ml), four peaks were observed before the peak of benzene appeared. Three of them were identified as *n*-heptane (≃0·15%), *cyclo*hexane (≃0·08%) and methyl*cyclo*hexane (≃0·07%), and their amounts were determined with diethyl ether as internal standard. The ratio of the peak height of the aliphatic hydrocarbons to that of ether is proportional to the ratio of their weights. K. Saito

3589. **Investigations on the relationship between gas-chromatographic ratios and vapour-pressure ratios. I. Aromatic hydrocarbons.** D. Jentzsch and G. Bergmann (Inst. f. Spektrochem. u. angew. Spektroskopie, Dortmund-Aplerbeck, Germany). *Z. anal. Chem.*, 1959, **165** (6), 401–415.—The gas-chromatographic retention ratios of aromatic hydrocarbons were measured at various temp. and were compared with the calculated vapour-pressure ratios; the Clausius - Clapeyron and Antoine formulae were utilised for the vapour-pressure calculations. Good agreement (to the first place of decimals) between the two ratios were obtained and the deviations occurring between these values are discussed with the aid of the Herrington equation. Diagrams of log retention ratio *vs.* log v.p., v.p. ratios and other functions are of value both for practical and theoretical applications. *o*-Xylene was used as the reference standard for the calculation of the retention and v.p. ratios.

G. P. Cook

3590. **Spot test for phenols by a modified indophenol method.** Takanobu Itai and Shozo Kamiya (Nat. Hygienic Lab., Tamagawa-yoga, Setagaya-ku, Tokyo). *Japan Analyst*, 1958, **7** (10), 616–618.—Autoxidation suffices for the formation of indophenols from *p*-aminophenol (**I**) (prep. described) and various phenols, including di- and tri-hydric phenols, *o*-, *m*- and *p*-amino- and *p*-chloro-phenols and naphthols, the colour produced being characteristic for each phenol. This test is as sensitive as that of Gibbs (*J. Biol. Chem.*, 1927, **72**, 649). Amines and sulphur compounds do not interfere. One drop of the sample soln. is mixed with one drop of NaOH soln. (2%) (and a few drops of ethanol when necessary) and **I** soln. (0·1 mg per ml, 0·5 ml). K. Saito

3591. **Gas chromatography of monohydric phenols.** J. Janák, R. Komers and J. Šíma (Lab. for Anal. of Gases, Acad. Sci., Brno, Czechoslovakia). *Chem. Listy*, 1958, **52** (12), 2296–2310.—The relation of the structure of the molecule in the solid phase to the selectivity of the separation of monohydric phenols is discussed. The specific elution vol. (chromatographic spectrum) of 19 phenols in polar and non-polar phases have been measured. In

practice, the use of Apiezon I or dimethylpolysiloxane has been found suitable for separation according to the C number, whereas the use of erythritol and the ethylene mercaptal of D-glucose is advantageous when separating according to the steric hindrance of the hydroxyl group. The temp. is kept between 150° and 170° during the separation. The reproducibility and accuracy of the areas under the chromatographic elution curve have been examined in relation to the weight and molar composition of the mixture, with H and N as carrier gases. J. ZÝKA

3592. **Spot tests for phenols and alkylated anilines based on the Duff formylation.** F. Feigl and E. Jungreis (Lab. Prod. Mineral, Min. da Agric., Rio de Janeiro, Brazil). *Analyst*, 1958, **83**, 666–669.—The formylation of phenols and dialkylanilines as developed by Duff (*J. Chem. Soc.*, 1941, 547; 1945, 226) has been extended to monoalkylanilines. It is effected by mixing in a micro test-tube a drop of the sample soln. in ethanol or diethyl ether with a mixture of crystalline oxalic acid and hexamine (1:1), warming to remove the solvent, heating the tube in a glycerol bath at 160° for 1 to 2 min. and adding a drop of a reagent made by dissolving 10 g each of hydrazine sulphate and Na acetate in 100 ml of water. The suspension (a drop of water may be added) is dried on filter-paper. If the sample contains phenols, the stains exhibit a blue - green or orange fluorescence in u.v. light. With phenol and cresols the *o*-hydroxyaldehydes formed volatilise, and a filter-paper moistened with the reagent is held over the melt. The failure of certain phenolic bodies to respond to the test is discussed. The procedure for the detection of mono- and di-alkylanilines is similar to that for phenols, except that the cooled reaction mixture is treated with one or two drops of water, and the soln. or suspension is placed on filter-paper impregnated with a soln. of benzidine in ether. An orange stain indicates a positive result. A. O. JONES

3593. **Metol (*p*-methylaminophenol sulphate) photographic grade.** British Standards Institution (2 Park Street, London). B.S. 3105: 1959, 12 pp.—Standards of quality are laid down, and apparatus and procedures specified for the determination of identity (melting-point of the nitroso derivative compared with that of an authentic specimen), volatile matter, ash, solubility in water, oxidisable matter, and iron and heavy metals by limit tests, and for the determination of *p*-aminophenol and the detection of *p*-di(methylamino)benzene.
E. J. H. BIRCH

3594. **Hydroquinone (quinol, *p*-dihydroxybenzene) photographic grade.** British Standards Institution (2 Park Street, London). B.S. 3103: 1959, 10 pp.—Standards of quality are laid down, and apparatus and procedures specified for the determination of melting-point, identity (mixed melting-point), ash, solubility in 5% acetic acid soln., oxidisable matter, and iron and heavy metals by limit tests.
E. J. H. BIRCH

3595. **An analytical method for the determination of the cresols, based on their capillary-active properties.** E. Angelescu and Y. Davidescu. *Stud. Cercet. Chim., Bucharest*, 1958, **6** (2), 213–231.—The proposed method for the determination of *o*-, *m*- and *p*-cresol in aq. soln. is based on the variation of surface tension when these isomers are titrated with NaOH soln. The curve of concn. of NaOH soln. against surface tension consists of parts. The first straight portion shows a linea increase of surface tension with increase of additio of NaOH, corresponding to the removal of cres molecules. The last portion shows a constant max value of surface tension when all the cresol has bee converted into the Na salt. The intermediat curved portion is due to the gradual dilution of th system and hydrolysis. The apparent end-point i obtained by the intersection of the projected straigh portions. Curves obtained with known concn. gav low results from stoicheiometric calculations whe the concn. of *o*-cresol was >0·7% and *m*-cres >0·35%. From these curves, empirical correctio factors were obtained which, for concn. up to 2·3 1·75 and 1·63% of *o*-, *m*- and *p*-cresol, respectively gave errors >0·8%. H. SHER

3596. **Physico-chemical investigation of — -phenyl acetylcarbinol [1-hydroxy-1-phenylpropanone] an methylbenzoylcarbinol [1-benzoylethanol]. II Polarographic determination of — -phenylacetylcar binol, methylbenzoylcarbinol and benzaldehyde i the presence of each other.** M. Fedoroňko (Dept Pharm. Chem., and Biochem., Chem. Inst. Acad Sci., Bratislava, Czechoslovakia). *Chem. Zvesti* 1958, **12** (12), 690–698.—The quant. polarographi determination of 1-hydroxy-1-phenylpropanone (**I**) 1-benzoylethanol (**II**) and benzaldehyde (**III**) ha been studied. Different $E_{\frac{1}{2}}$ values in the mediu of 0·5 *M* aq. $NH_3$ with 0·5 *M* $NH_4Cl$ permitted th determination of **II** or **III** in the presence of **I** By using a soln. in a mixture of 0·025 *M* methyl amine and 0·11 *M* methylamine hydrochlorid (pH 10), the determination of **III** (after conversio to a Schiff's base) in the presence of **II** (which doe not react with methylamine) can be carried out *Procedure*—Add a 1% ethanolic soln. of the sampl (0·5 ml) to the buffer soln. (0·5 *M* aq. $NH_3$ - 0·5 *M* $NH_4Cl$) (3·5 ml), remove O with a stream of N and immediately register the polarographic wave Compare with a calibration curve. J. ZÝKA

3597. **Colorimetric determination of (−)-phenyl acetylcarbinol.** O. Bauerová and Š. Bauer (Dept Pharm. Chem. and Biochem., Chem. Inst. Acad Sci., Bratislava, Czechoslovakia). *Chem. Zvesti* 1959, **13** (1), 38–41.—(−)-Phenylacetylcarbinol (**I** reacts with blue tetrazolium (**II**) yielding a colou suitable for analytical purposes. The method i not influenced by the presence of benzaldehyde an can be used in controlling technological products o **I** with an accuracy of ±3%. *Procedure*—Into 50-ml flask place an ethanolic soln. of the sampl ($10^{-5}$ to $10^{-6}$ g of **I**), add 1 ml of freshly prepared **I** soln. (0·2% ethanolic), 1 ml of 0·05 *N* NaOH i 25% *iso*propyl alcohol and set aside for 10 to 1 min., with occasional shaking. Dilute to vol. wit a soln. of 0·01 *N* acetic acid in 90% *iso*propyl alcoho and measure the extinction with the use of a blue green filter (490 mμ). J. ZÝKA

3598. **Detection of arylidene arylhydrazones an thereby differentiation of aromatic aldehydes an ketones.** E. Sawicki, T. W. Stanley and T. R Hauser (R. A. Taft San. Engng Center, U.S. Dept of Health, Education and Welfare, Cincinnati Ohio, U.S.A.). *Chemist Analyst*, 1958, **47** (4), 87–88 —To a few ml of a soln. of a hydrazone in 2-meth oxyethanol (**I**) add 0·1 ml of a fresh 0·5% soln. o *p*-nitrophenyldiazonium fluoroborate in **I**, followe by 0·2 ml of 10% aq. tetraethylammonium hydrox ide soln. Dilute the mixture to 10 ml with **I** note the colour, and determine the absorptio

ectrum from 400 to 700 mμ against the appro- ate blank. Colours, wavelengths of maximum sorption, and sensitivities are listed for 10 mpounds. All arylidene arylhydrazones tested, cept those containing pyridine rings or nitro or ino groups, gave purple, blue or green colours, ile hydrazones from all arylalkyl, dialkyl and ryl ketones gave a (negative) yellow colour. the reaction is carried out in a micro test-tube th one-twentieth of these quantities of reagents, sitivities of the order of 0·1 μg can be obtained, d the same order of sensitivity is attained in a er-paper spot-test procedure. R. E. Essery

3599. **Potentiometric titrations of weak acids in n-aqueous solvents. I. Benzoic acid, ϵ-cyclo-xylcaproic acid, *p*-cresol and 1-naphthol.** D. H. athews and T. R. Welch (British Petroleum Co., d., Sunbury-on-Thames, Middx, England). *J. ppl. Chem.*, 1958, **8** (11), 701–710.—Potassium ethoxide (0·1 *N*), standardised with benzoic acid, used for the titration of organic acids such as cur in bitumens and tars. Benzene - methanol :1), benzene - *iso*propyl alcohol (3:1), or acetone suitable for carboxylic acids, the first being pecially so; the presence of phenols makes the d-point less sharp. For acid - phenol mixtures, hylenediamine - benzene (3:1) or *n*-butylamine is ed; $CO_2$ in solvents is neutralised with K meth- ide before titration. The electrode system atinum - tungsten was selected, isolation of the ference electrode being necessary to avoid reversal the slope of the titration curve near the neutral- ation point. The e.m.f. ($E$) *vs.* vol. of titrant ($V$), d subsequently $V$ *vs.* $dE/dV$ are plotted to give e end-point. The antimony - platinum electrode stem is suitable for titrations in ethylenediamine - nzene. Reproducibility is ±1·25% of $V$ for the st three solvents, but rather poorer for the two sic solvents. Indicator titrations of similar ixtures are somewhat more precise.

**II. Hydroxybenzoic acids and dihydric phenols *n*-butylamine.** D. H. Mathews and T. R. Welch. *id.*, 1958, **8** (11), 710–715.—The carboxyl and ydroxyl groups of hydroxybenzoic acids can be trated accurately with K methoxide in *n*-butyl- mine if the antimony - glass electrode system is ed. The hydroxyl groups of dihydric phenols n also be determined, except for the second ydroxyl group in 4-methylcatechol. The plati- m - tungsten electrode system is suitable for the termination of the carboxyl group only. Acids trated include salicylic acid, *p*-hydroxybenzoic id, 2:4- and 2:5-dihydroxybenzoic acid; dihydric henols used were resorcinol, quinol, 3-methyl- techol, 4-methylcatechol, and 1:5- and 1:6- hydroxynaphthalene. The effect of the substitu- on position is discussed; groups in *ortho* positions crease the dissociation of the carboxyl group, and ssen that of the hydroxyl group, while the reverse true for *para* substitutions. For the *meta* position marked effects are observed.

P. D. Parr-Richard

3600. **Oxidative metabolism of phenylacetic acid by *enicillium chrysogenum* A176. XIV. Biological termination of *p*-hydroxybenzoic acid.** Masao ono (Inst. for Fermentation, Juso-nishinocho, igashiyodogawa-ku, Osaka). *J. Agric. Chem. c. Japan*, 1958, **32** (6), 433–435.—*p*-Hydroxy- nzoic acid (**I**) is determined biologically with a rain of *Pseudomonas*, by the use of a Warburg anometer. The method is similar to that for enylacetic acid (*Ibid.*, 1953, **27**, 193). A linear relationship holds between the concn. of **I** and the vol. of evolved O. Protocatechuic acid interferes, but benzoic, salicylic, *m*-hydroxybenzoic and gentisic acids, phenol and catechol do not.

K. Saito

3601. **Reactivity of catecholamines, 5-hydroxy-indoles and phenols with blue tetrazolium.** H. Rosenkrantz (Worcester Foundn. for Exp. Biology, Shrewsbury, Mass., U.S.A.). *Arch. Biochem. Biophys.*, 1959, **81** (1), 194–203.—A comparative study is made of the reaction rates and intensities of 27 compounds with blue tetrazolium (**I**) and with the $FeCl_3$ - 2:2′-dipyridyl reagent (**II**) of Emmerie and Engel. The reactivity of catecholamines with **I** was about four times that of 5-hydroxy-indoles or α-ketolic steroids, and an adaptation of the test to the assay of urinary catecholamines is described. Although less sensitive, the reaction with **II** was of value in distinguishing catechol-amines from the corresponding N-methylated derivatives.

W. H. C. Shaw

3602. **Spectrophotometric determination of stabil-ised diazonium compounds.** H. M. Rosenberger and C. J. Shoemaker (A. B. Dick Co., Chicago, Ill., U.S.A.). *Anal. Chem.*, 1959, **31** (2), 204–206.—The absorption spectra of the diazonium com-pounds investigated show strong absorption bands in the 350 to 400-mμ region, which are attributed to the –N:N– chromophore group. The max. at 380 mμ obeys Beer's law in the concn. range 1 to 10 p.p.m. The sample is measured in aq. soln. The results agreed within 1% with those obtained by the nitrometer procedure, and the method was successfully applied to wax mixtures (used as paper-coating materials).

G. P. Cook

3603. **Paper chromatography of aromatic nitro compounds.** M. Perpar, M. Tišler and Ž. Vrbaški (Inst. f. organ. Chem., Univ., Ljubljana, Yugo-slavia). *Mikrochim. Acta*, 1959, (1), 64–67.—Filter-paper (S. & S. 2043b) is impregnated with a petroleum fraction (boiling-range 160° to 190°) and allowed to dry for 30 min. in air; 0·05 ml of a 0·1% ethanolic soln. of the sample is spotted on the paper and developed for 12 to 15 hr. at 24° with either 96% ethanol - water (4:3) or 96% ethanol - water (3:5). $R_F$ values are quoted for 18 aromatic nitro compounds. In some cases the com-pounds were eluted completely and the eluate examined spectrophotometrically; for amounts of 2 to 6 μg, recoveries with a precision of ±5% are quoted. In other cases the errors were too high for the method to be of practical use.

T. R. Andrew

3604. **Infra-red analysis of the isomers of NN-diethyltoluamide.** W. H. Clark (Hercules Powder Co., Wilmington, Del., U.S.A.). *Anal. Chem.*, 1959, **31** (2), 197–199.—Two procedures are des-cribed: one for mixtures containing a high *m*-isomer content (60 to 90%), a low *p*-isomer content (10 to 40%) and no *o*-isomer, and the other proced-ure is applicable to *o*-isomer concn. of 5 to 10%. The *m*- and *p*-compounds are determined by conventional i.r. techniques but a compensation procedure is used for the *o*-compound to reduce interference by the *m*-isomer. The precision for the first method (95% confidence limits) is ±0·8% absolute for duplicate determinations of a mixture containing 85 and 15% of the *m*- and *p*-isomers, respectively; recoveries are >99 and >98%,

respectively. The precision for the determination of the *o*-isomer is ±0·2% absolute at a concn. of 5%; recoveries are >92%. G. P. Cook

3605. **Fluorescence of some salicyloyl hydrazones.** P. S. Chen, jun. (Nat. Heart Inst., Nat. Inst. of Health, Bethesda, Md., U.S.A.). *Anal. Chem.*, 1959, **31** (2), 296–298.—*o*-Hydroxybenzaldehyde, *p*-hydroxybenzaldehyde and *p*-dimethylaminobenzaldehyde form salicyloyl hydrazones with fluorescence characteristics that are relatively specific compared with those of other salicyloyl hydrazones, which either do not fluoresce or do so with excitation and fluorescence maxima similar to those of salicyloyl hydrazine. The maximal excitation of the three compounds occurs at 390 mμ and the fluorescence at 470 mμ, as compared with 350 and 425 mμ for salicyloyl hydrazine.
G. P. Cook

3606. **Determination of small amounts of 2-naphthylamine in 1-naphthylamine.** G. Parravano (ACNA, Cegnio, Italy). *Chim. e Ind.*, 1959, **41** (1), 30–33.—The method described is based on the colorimetric reaction of furfuraldehyde with primary aromatic amines. The conditions under which the reaction rate is lowest for the 1- and highest for the 2-isomer are established [in ethanol (25 ml) with dil. acetic acid (0·5 ml) at 20° for ≯90 min.] and a quant. determination is developed which is based on extinction measurements at 550 mμ. A suitable calibration curve is given. Data are plotted for 1-naphthylamine containing 0·5, 5·0 and 10% of the 2-isomer. The method can also be applied to nitronaphthalenes, after reduction to the amines. C. A. Finch

3607. **Physical properties of anthraquinone and its derivatives. I. Infra-red spectra.** H. Bloom, L. H. Briggs and B. Cleverley (Dept. of Chem., Univ. of Auckland, New Zealand). *J. Chem. Soc.*, 1959, 178–185.—The infra-red spectra of 60 anthraquinone derivs. are listed, and the reason for differences in absorption is discussed. A summary of diagnostic features is given, showing that the spectrum of an individual compound is unique. E. J. H. Birch

3608. **Colorimetric determination of (+)-pulegone with 3:5-dinitrobenzoic acid.** D. H. E. Tattje (Rijksuniv., Gronigen, Netherlands). *Pharm. Weekbl.*, 1958, **93** (24), 1048–1053.—*Procedure*—To 4 ml of a soln. containing 0 to 2·7 mg of (+)-pulegone in ethanol add a 4% soln. of 3:5-dinitrobenzoic acid in ethanol (5 ml) and 3 *N* aq. NaOH (2 ml). Set aside for 40 min. and measure the extinction at 5375 A against a reagent blank. The calibration curve conforms to Beer's law up to 2·7 mg of (+)-pulegone. The temp. must be maintained at 20° for all determinations. With two out of three samples of pennyroyal oil, both of higher density than (+)-pulegone and darker than the third sample, the colorimetric method gave lower results than the neutral sulphite method. With the third sample and with pure (+)-pulegone, the results of the two methods were in good agreement. Piperitone and piperitenone, which may also occur in pennyroyal oil, give the same reaction. Menthone does not react with 3:5-dinitrobenzoic acid. G. Burger

3609. **Pyridine.** British Standards Institution (2 Park Street, London). B.S. 3096–97:1959, 16 pp.—Standards are laid down for pyridine (99% minimum purity; B.S. 3096) and pyridine (90% minimum purity; B.S. 3097). Apparatus and procedures are specified for the determination of colour, distillation range, residue on evaporation, miscibility with water, and clearing-point.
E. J. H. Birch

3610. **Pyridine bases.** British Standards Institution (2 Park Street, London). B.S. 3098–99:1959, 20 pp.—Specifications are laid down for pyridine bases, 90/160 (B.S. 3098) and 95/180 (B.S. 3099). Apparatus and procedures are specified for the determination of colour, distillation range, water, total bases, non-basic material other than water, and primary bases, and for tests for miscibility with water and 95% (v/v) ethanol, and for pptn. with cadmium chloride and for the colour of the ppt. with Nessler reagent. E. J. H. Birch

3611. **Determination of pyridine-2-aldoxime methiodide and its corresponding stereoisomer by ultraviolet analysis.** E. I. Ellin and A. A. Kondritzer (Army Chem. Center, Md., U.S.A.). *Anal. Chem.*, 1959, **31** (2), 200–201.—A method for the determination of pyridine-2-aldoxime methiodide (**I**) in the presence of its acid hydrolytic products is based on the fact that the *anti*-isomer exhibits absorption maxima at 292 mμ in acid soln. and at 333 mμ in alkaline soln. Neither the *syn*-isomer nor the acid hydrolytic products of **I** interfere at these wavelengths. The accuracy is ≃100% in the concn. range of 0 to 10 μg per ml. Because **I** yields hydroxylamine on acid hydrolysis, the formation of pyridine-2-carboxaldehyde methiodide (**II**) was indicated and the spectrum of this compound was also investigated. Determinations of **II** gave recoveries ≃100% in the 1 to 10-μg range.
G. P. Cook

3612. **Phosphorescence spectra and analysis of some indole derivatives.** S. Freed and W. Salmre (Chem. Dept., Brookhaven Nat. Lab., Upton, N.Y., U.S.A.). *Science*, 1958, **128**, 1341–1342.—A rotating phosphoroscope between two monochromators disposed at right angles is employed to measure the spectra of soln. frozen at low temp. (77° K). The method is superior to spectrofluorimetry, some indole derivatives indistinguishable by their fluorescence being easily differentiated by phosphorescence measurements. H. F. W. Kirkpatrick

3613. **Studies on furfuraldehyde. VI. The colorimetric determination of furfuraldehyde with aniline in the presence of some mineral acids.** D. A. Isăcescu, S. Biller and M. Macavei-Beştelei. *Stud. Cercet. Chim., Bucharest*, 1958, **6** (2), 247–253.—In previous work (*cf.* Isăcescu and Biller, *Stud. Cercet. Biochim.*, 1958, **1**, 2) it was observed that ethanolic soln. of aniline and furfuraldehyde (**I**) gave a rose-red colour which followed the Beer - Lambert law. The conditions for determinations of **I** with a Duboscq type of colorimeter have been investigated. *Procedure*—An ethanolic soln. of aniline (1 *M*) (4 ml) and **I** soln. (4 ml) is treated with 0·02 ml of HCl, $H_2SO_4$ or $H_3PO_4$ (0·01 *N*). The rose-red soln. is warmed for 1 min. on the water bath, then cooled, and left at room temp. for 30 min. The colour is then compared with a standard. Standard soln. recommended are 4 ml of **I** soln. (0·1%) for concn. of 0·2 to 0·5% in a 20-mm tube (1% for concn. of 2 to 3% in a 10-mm tube). For 1 ml of a standard of 0·1% good results are obtained with concn. between 0·05 and 0·5% at a depth of 5 mm. A preliminary trial with a standard soln. is necessary

establish whether the unknown soln. must be ted so that the subsequent colour developed s within the range of the standard.

H. Sher

614. **Determination of closed flash-point of oleum products by means of the Pensky-Martens aratus.** British Standards Institution (2 Park eet, London). B.S. 2839:1957 (Amendment No. ub. 10.4.59), 2 pp.—The amendments include rence to I.P.34/58 and changes in the dimen- al limits of the apparatus, in the precision and he specification of the thermometers. Clause he preparation of the sample, is omitted.

G. Burger

615. **Separation of paraffin - cycloparaffin portion aphtha into normal, branched and cycloparaffins.** S. Norris and J. G. O'Connor (Gulf Res. and elopment Co., Pittsburgh, Pa., U.S.A.). *Anal. m.*, 1959, **31** (2), 275–279.—The saturate fraction a naphtha was charged on a column of 5-A ecular sieves. The branched and cyclic com- ents were eluted with *iso*pentane and the ight-chain compounds removed with *n*-pentane. branched and cyclic material was separated by omatography using a high pore-volume silica saturated with 2-(2-methoxyethoxy)ethanol. column was eluted with a perfluorocyclic ether $F_{16}O$), the branched material being eluted first high purity and the cyclic compounds last, rmediate fractions showing decreasing contents branched and increasing contents of cyclic pounds.

G. P. Cook

616. **Mass-spectrometric analyses of medium- osity lubricating oils.** M. L. André and M. J. eal, jun. (Res. Lab., Shell Oil Co., Houston, ., U.S.A.). *Anal. Chem.*, 1959, **31** (2), 164–169.— en representative medium-viscosity oils have n examined by mass spectrometry and the tion of the *iso*alkane and condensed and non- densed *cyclo*alkane content to the viscosity ex determined. An examination has been made he relation of the depth of extraction of the oil n furfuraldehyde to the aromatic content of the nate.

K. A. Proctor

617. **Insulating oil for transformers and switch- r.** British Standards Institution (2 Park Street, don). B.S. 148:1959, 40 pp.—This Standard aces B.S. 148:1951. The evaporative loss test eleted. The procedure for acidity determination been improved by substituting ethanolic KOH aq. KOH. An appendix on thermometer cifications is included. The standard applies to sed insulating oils, and not to high-viscosity cable and capacitor oils or impregnating oils.

G. Burger

618. **Spectrophotometric analysis of distillable -temperature tar bases.** C. Karr, jun., and Ta- ang Lo Chang (Low-temp. Tar Lab., Bur. of es, Morgantown, W. Va., U.S.A.). *J. Inst. Fuel*, 8, **31**, 522–527.—Bases amounting to 0·31% w) of a low-temp. (480° to 510°) tar from a high- tile bituminous coal were separated by vacuum tionation (125° and 0·133 mm) and acid extrac- (*cf.* Fisher and Eisner, *Ind. Eng. Chem., Anal.* 1937, **9**, 213) and divided into 35 fractions by llation at 25° to 186° at 80 mm to 3 mm. parison of the u.v. and i.r. absorption spectra he fractions with those of pure compounds wed the presence of 17 pyridine derivatives (*P*) amounting to 35% (w/w) of the bases, 23 quinolines (*Q*) (46%), and 11 anilines (*A*) (16%). Besides alkyl (mainly methyl) homologues, *P* included *cyclo*penteno- and phenyl-pyridines; *Q* included benzoquinolines, and *A* included N-benzylanilines and 2-naphthylamine.

A. R. Pearson

3619. **Methods for the analysis and testing of coal and coke. Part 7. Ultimate analysis of coke.** British Standards Institution (2 Park Street, London). B.S. 1016: Part 7:1959, 36 pp.—In this Standard, which deals with the determination of C, H, N and S, the Liebig method for the determination of C and H has been modified and an alternative method introduced. A semi-micro method has been substituted for the macro-Kjeldahl method for N, and the Eschka method for total S has been modified. The section on preparation of the sample has been transferred to the revised B.S. 1017.

G. Burger

3620. **Methods for the analysis and testing of coal and coke. Part 11. Forms of sulphur in coal.** British Standards Institution (2 Park Street, London). B.S. 1016:Part 11:1959, 13 pp.—This Standard deals with the determination of sulphate, and pyritic and organic S. The method of Powell and Parr (*U.S. Bur. Mines Tech. Paper No.* 254) has been modified. Pyritic S is obtained from the determination of total iron and non-pyritic iron. Organic S is determined by difference. The section on the preparation of the sample has been transferred to B.S. 1017.

G. Burger

3621. **Sampling and testing gelatins.** British Standards Institution (2 Park Street, London). B.S. 757:1959, 47 pp.—The methods for initial and final sampling of sheet, cake, leaf, pearl, powdered, granulated, flake and kibbled gelatin, and for the preparation of the laboratory sample, are laid down. Procedures and apparatus are specified for the determination of moisture, jelly strength (finger test and Bloom-type gelometer), viscosity, melting-point, water absorption, solubility of partially swollen sheet, keeping quality, pH, grease, ash, $SO_2$, chlorides, arsenic, heavy metals, lead, copper and zinc.

E. J. H. Birch

3622. **Sampling and testing glues.** British Standards Institution (2 Park Street, London). B.S. 647:1959, 37 pp.—Methods are given for the initial and final selection of the sample, and the preparation of the laboratory sample, for sheet, cake, powdered, pearl, cube, granulated, flake, and kibbled glues, and slab, jelly and liquid glues. Methods and apparatus are specified for the determination of moisture, jelly strength (finger test and Bloom-type gelometer), viscosity, melting-point, water absorption, foam, keeping quality, pH, grease, ash, $SO_2$, chlorides, and joint strength in shear.

E. J. H. Birch

3623. **Physicochemical characterisation of essential-oil constituents and their derivatives by modern instrumental techniques.** L. Levi, J. L. Thomson, J. C. Evans, H. Bernstein, S. A. Forman and N. M. Miles (Food and Drug Lab., Dept. of Nat. Health and Welfare, Ottawa, Canada). *Perfum. Essent. Oil Rec.*, 1958, **49** (11), 715–728.—The application of physicochemical methods to the analysis of essential oils is discussed, with a survey of relevant literature. Figures for the conventional physicochemical constants are tabulated, and i.r. and Raman spectra data are given for eugenol, its methyl and acetyl

ethers, *iso*eugenol, its methyl, acetyl and benzyl ethers, and anethole. X-ray powder diffraction data are recorded for *iso*borneol, (−)-borneol, *iso*bornyl, (±)-bornyl and (−)-bornyl *p*-nitrobenzoates, the 2:4-dinitrophenylhydrazones of (±)-camphor and (−)-camphor, (±)-camphor semi carbazone, and (±)- and (−)-pinonic acids, by using film and diffractometer methods, with cobalt radiation and iron filter. The results for the various compounds, and the advantages and limitations of the different techniques for their characterisation and identification, are discussed.
R. E. Essery

3624. **Identification of colouring matters by paper chromatography. Various applications.** Z. Molester. *Ann. Chim., Paris,* 1958, **3** (11–12), 771–814.—After a preliminary literature survey, apparatus is described for the paper chromatography of synthetic organic dyes by the ascending technique at room temp. Eighty-five dyes, in 13 different chemical groups, were examined, with several solvent systems, and for each dye the following data are given—concn. of dye (0·1 to 0·25% aq. or alcoholic), most suitable solvent system, duration of chromatography (1·5 to 7 hr.), $R_F$ value, colour of the spot in daylight and u.v. light before and after chromatography, and colour of the spot in daylight after treatment with 10% NaOH soln. and 10% HCl. The applications described, with manipulative details, include the comparison and identification of the colouring matters of lipsticks and lipstick stains, and the investigation of the colouring matters of liquid inks and those used in ball-point pens and of specimens of writing produced therewith. R. E. Essery

3625. **Bromination as a method for the analysis of triphenylmethane dyes.** M. Matrka (Res. Inst. Org. Synth., Pardubice-Rybitví). *Chem. Průmysl,* 1958, **8** (11), 583–585.—A 0·2 *N* bromate - bromide soln. (5·568 g of $KBrO_3$ plus 24 g of KBr in 1 litre) is used for the direct potentiometric determination of triphenylmethane dyes. *Procedure*—Dissolve the sample (0·1 g) in *N* HCl (100 ml) and titrate potentiometrically, with stirring, with 0·2 *N* $KBrO_3$ - KBr. Near the end-point the dye is pptd. The method is suitable for the determination of pure triphenylmethane dyes. The presence of compounds that readily react with bromine (*e.g.*, leuco-bases, intermediates such as Michler's ketone, Michler's hydrol and 4:4′-tetramethyldiaminodiphenylmethane) causes results higher than those obtained by another reductimetric determination with $VSO_4$, and the use of the procedure described is therefore limited. It is, however, useful for determining the leuco-bases of various dyes, *e.g.* malachite green. The mechanism of the bromination is discussed. J. Zýka

3626. **Determination of cellulose, and indirectly of household coal, in compost from town refuse.** L. J. Mebius (Inst. voor Bodemvruchtbarheid, Gronigen, Netherlands). *Chem. Weekbl.,* 1958, **54** (50), 711–715.—Samples are prepared by boiling the dried and ground compost (300 mg) with 80 ml of Scharrer - Kurschner reagent [70% aq. acetic acid containing 27·5 g of trichloroacetic acid and 68 ml of $HNO_3$ (sp. gr. 1·4) in 1 litre]. The residue is washed with reagent, water and acetone, dried and weighed. Cellulose is determined by heating one sample for 90 min. in a boiling-water bath with 15% (w/w) aq. $H_2SO_4$ (40 ml) and 2 *N* $K_2Cr_2O_7$ (25 ml), mixing 25 ml of the soln. with 0·22 *N* $FeSO_4$ (25 ml) and titrating the excess with 0·1 *N* $KMnO_4$. The coal content is then determined from the loss on ignition of a second prepared sample.
G. Burger

3627. **Determination of nitrogen in nitrocellulose** J. D. Mullen (African Explosives and Chem Industries Ltd., Transvaal, S. Africa). *Anal. Chim Acta,* 1959, **20** (1), 16–19.—An examination of th transnitration method of Stalcup and William (*cf. Anal. Abstr.,* 1955, **2**, 2468) indicated that th precision could be improved by altering the con ditions of reduction. With the modified procedure a series of ten determinations on a sample of KNO containing 13·8% of N gave a standard deviatio of ±0·014. W. T. Carter

3628. **Rapid determination, without a nitrometer of nitrogen for control of manufacture of nitro cellulose.** O. Frehden and Z. Nicolescu. *Rev Chim., Bucharest,* 1958, **9** (12), 688–689.—Th method consists in saponification of the nitro cellulose, reduction of the $HNO_3$ to $NH_3$, and it subsequent titration after distillation, these opera tions taking place in a special apparatus (illustrated) *Procedure for micro- or semi-micro determinations*— Nitrocellulose (5 to 10 mg, or 50 to 100 mg) i transferred to the reaction vessel by means of small amount of a mixture of diethyl ether an ethanol or acetone; 5 to 15 ml of NaOH soln. (30% and 0·5 to 2 ml of $H_2O_2$ (30%) are added, the funne tap is closed and steam is passed in to the jacket o the reaction vessel. When the nitrocellulose i dissolved, 0·5 to 1 g of Devarda's alloy is washed i through the funnel with a little water, followed b more NaOH soln. The liberated $NH_3$ is distille into 2% $H_3BO_3$ and titrated with 0·02 *N* $H_2SO_4$ with methyl red (0·1% in ethanol) or a mixture o 3 parts of bromocresol blue soln. (0·1%) and part of methyl red soln. (0·1%), both in ethano as indicator. The results are consistently 0·10 t 0·13% higher than those from nitrometer deter minations. H. Sher

3629. **Quantitative analysis of binary fibre mixture containing Tricel (cellulose triacetate).** W. Armfiel (Courtaulds Ltd., Droylsden, Manchester). *J Text. Inst. Proc.,* 1959, **50** (1), P51–P55.—The fibr groups investigated are—wool, cotton, polyamid (nylon 66), polyester (Terylene), regenerate protein (Fibrolane BX), acrylic (Courtelle an Orlon 42), viscose rayon (Fibro), and secondar cellulose acetate (Dicel). In fibre mixtures o Tricel with Dicel, the latter is dissolved by extractio with 70% v/v aq. acetone; Tricel is removed fro all the other mixtures by extraction with dichlor methane. O. M. Whitton

3630. **Colorimetric determination of sulphur i rayon staple, cellulose acetate and poly(vinyl alcohol)** Hiroshi Terada and Masao Yosida (Otake Plan Mitsubishi Rayon Co., Otake, Hiroshima-ken *J. Chem. Soc. Japan, Ind. Chem. Sect.,* 1958, **6** (10), 1301–1303.—The phosphoric acid - stannou chloride method (*cf.* Kiba *et al., Anal. Abstr.,* 195 **5**, 1874) followed by colorimetric determination o resulting $H_2S$ with 4-aminodimethylaniline (**I**) wa applied to the analysis of S in rayon staple, cellulos acetate and poly(vinyl alcohol). Conversion of into $SO_4^{2-}$ is effected by heating with $HNO_3$ an MgO. The standard deviation is ±0·0003% fo ≃0·02% of S and the time taken for an estimation ≃1 hr. *Procedure*—Wash the sample (1 g) with ho water (to remove oily substances), dry and mix

-g portion with MgO (50 mg) and $HNO_3$ (2 ml) in a ss vessel and heat first on a sand bath and then an oven (700° to 800°) for 10 min. until nitrate is npletely decomposed. Add conc. phosphoric d (5 ml) containing $Cr^{3+}$ and $Sn^{2+}$. [Heat $H_3PO_4$ ler reduced pressure to 300°. Add $K_2Cr_2O_7$ g) to the phosphoric acid (300 g), heat until the uid becomes green, cool and add $SnCl_2$ (50 g) h heating to 300°.] Heat to 300° in a current $CO_2$ (60 to 120 bubbles per min.) for 15 min. l pass the $H_2S$ into Zn acetate (4%, 35 ml). ol for 5 min. in a current of $CO_2$. Add **I** hydroride (0·5% in 500 ml of 18 *N* $H_2SO_4$ containing nl of 6 *N* HCl) (1 ml) and $FeCl_3$ (10%, 1 ml) to Zn soln., keep at 5° to 25° for 15 min., dilute to nl and measure the extinction at 655 m$\mu$.

K. Saito

3631. **Quantitative chemical analysis of mixtures viscose rayon and cotton.** British Standards stitution (2 Park Street, London). B.S. 3068: 59, 7 pp.—The apparatus and procedure are scribed for the extraction of viscose rayon from xtures with unscoured, scoured, kiered or bleached tton with sodium zincate soln. The residue, rrected for loss in the solvent, is expressed as a rcentage by weight of the sample, the viscose yon being obtained by difference. The calculan of the results on the basis of dry weight or rrect invoice weight is described. The accuracy the results is discussed in relation to the proporn and nature of the cotton in the mixture.

A. M. Spratt

3632. **Quantitative chemical analysis of binary xtures of nylon 6 or nylon 66 and certain other res.** British Standards Institution (2 Park St., ndon). B.S. 3069:1959, 6 pp.—The apparatus d procedure are specified for the extraction of lon from mixtures with cotton, viscose rayon, lyester fibre and wool (<25% of wool) with 80% rmic acid. The residue, after correction for loss the solvent, is expressed as a percentage by wt. the mixture, and nylon is obtained by difference. e calculation of the results on the dry weight and rrect invoice weight is described.

A. M. Spratt

3633. **Method for the determination of conductty, pH, water-soluble matter, chloride and sulphate aqueous extracts of textile materials. Tentative xtile standard No. 52.** Textile Institute. *J. xt. Inst., Proc.*, 1958, **49** (12), P724–P731.—pparatus and procedures are specified.

3634. **Spectrophotometric determination of styrene a styrene - methyl methacrylate copolymer.** V. Tobolsky, A. Eisenberg and K. F. O'Driscoll rinceton Univ., N.J., U.S.A.). *Anal. Chem.*, 59, **31** (2), 203–204.—Styrene is determined by easuring the absorbance of 1 mg of the copolymer $CHCl_3$ soln. at 269 m$\mu$. The absorbance is linear ly up to ≃40% of styrene. G. P. Cook

3635. **Condensation of silicone resins (determination of silanol groups).** W. Noll, K. Damm and Krauss (Farbenfabr. Bayer Akt., Leverkusen, Germany). *Farbe u. Lack*, 1959, **65**, 17–24.—e resin, dissolved in chlorobenzene or dioxan, is ated under reflux for 2 hr. with *iso*cyanatobenzene, excess of which is then caused to react with butylamine, and the residual amine is titrated h HCl. This method will determine OH present $H_2O$ as well as OH in silanol groups. To disguish between the two types, a Karl Fischer determination is carried out; $H_2O$ reacts immediately but silanol groups only slowly.

L. A. O'Neill

3636. **Applications of infra-red spectroscopy in paint analysis and paint chemistry.** A. Reuter (Battelle Inst., Frankfurt/Main, Germany). *Farbe u. Lack*, 1959, **65**, 25–36.—Examples of the uses of infra-red spectroscopy in the following problems are given, with illustrative spectra—analysis of solvent mixtures; identification of vinyl polymers and polyesters; examination of insoluble films (*e.g.*, of polybutadiene, phenolic and urea resins, after initial pyrolysis); the mechanism of curing of polyurethanes; changes following high-energy irradiation of polyethylene. L. A. O'Neill

3637. **Methods of testing raw rubber and unvulcanised compounded rubber. Part 2. Methods of chemical analysis.** British Standards Institution (2 Park Street, London). B.S. 1673, Part 2:1954 (Amendment No. 3, pub. 10.2.59), 10 pp.—The amendment specifies procedures for the determination of Mn in natural raw rubber, and of Cu (<10 p.p.m.) in raw and unvulcanised compounded rubber using a wet-oxidation method and in natural raw rubber by dry-ashing (two methods).

B. B. Bauminger

3638. **Methods of testing vulcanised rubber. Part B17. Determination of total copper.** British Standards Institution (2 Park Street, London). B.S. 903:Part B17:1959, 7 pp.—The determination of trace amounts of Cu is based on a wet oxidation of 2 g of sample with conc. $H_2SO_4$ and $HNO_3$. Iron is complexed with ammonium citrate and, after making ammoniacal, the soln. is shaken with a measured amount of a $CHCl_3$ soln. of Zn diethyldithiocarbamate. The yellow $CHCl_3$ layer is transferred to a stoppered flask containing anhyd. $Na_2SO_4$ and its extinction is measured at 435 m$\mu$. A reagent blank is carried out side by side with the test. The preparation of a calibration graph is described. B. B. Bauminger

3639. **Methods of testing vulcanised rubber. Part B19. Preparation and examination of water extract.** British Standards Institution (2 Park Street, London). B.S. 903:Part B19:1958, 8 pp.—The method consists in boiling the rubber sample with water for 1 hr.; the water extract is used for the determination of total water-soluble matter, free acid or alkali, chloride, sulphate, pH value, electrical resistivity of the extract and a test for the presence of ammonium salts. The procedures specify a test portion of 5 to 15 g of the prepared sample and require an amount of water 20 times the weight of the test portion. The total minimum vol. of water required for all tests is 95 ml.

B. B. Bauminger

3640. **Methods of testing vulcanised rubber. Parts G1 to G9. Methods of testing rubber proofed fabric.** British Standards Institution (2 Park Street, London). B.S. 903:Parts G1 to G9:1957, 34 pp.—General purpose tests which are regarded as common to all types of proofing are described, *i.e.*, selection of samples and test pieces; weight of proofing; state of vulcanisation (heat-cured and cold-cured vulcanisates); adhesion of proofing layers (ply and face adhesions); waterproofing (low- and high-pressure methods); breaking strength in tension; water extract; accelerated ageing (oven and oxygen pressure methods); and bend modulus stiffness. B. B. Bauminger

3641. **Colorimetric method for determination of protein in casein.** A. Marchenko (Tech. School, Chashinsk). *Molochnaya Prom.*, 1957, **18** (12), 28–29.—The use of the biuret test for the determination of protein in technical casein is described. Place ≃0·5 g of casein in a 50-ml beaker with 5% NaOH soln. (30 ml) and stir every 3 to 4 min. After 20 to 25 min., place the beaker in water at 45° to 50° and stir the mixture every 2 to 3 min. until either a colloidal soln. or a uniform mass of fine casein flakes is formed (usually 5 to 10 min., and 20 to 25 min. is required to dissolve acid and rennet casein, respectively). Transfer the mixture to a 50-ml flask and dilute to vol. Mix thoroughly and quickly pipette 2 ml of the soln. into a test-tube. Add water (8 ml), mix, add 5% $CuSO_4$ soln. (1 ml), mix again and then add 30% NaOH soln. (1 ml). Mix thoroughly for 1 min. and allow to stand for 1·5 hr. Read the clear violet - blue supernatant liquid in a colorimeter with casein standards closest in colour to the unknown. The method gives results in good agreement with those for the Kjeldahl method. CHEM. ABSTR.

3642. **Infra-red quantitative analysis data.** *Anal. Chem.*, 1959, **31** (2), 316.—The following data are given. **Determination of 2-nitronaphthalene in 1-nitronaphthalene,** R. E. Seeber, J. L. Alexander and H. J. McCarthy. **Determination of 2-naphthol in 1-naphthol,** R. E. Seeber and R. G. White.

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*See also Abstracts*—**3370**, Analytical use of diarylborinic acids. **3393**, Determination of $H_2O$ in organic solvents. **3425**, Determination of Al and Ti in polyethylene. **3444**, Determination of mandelic and *p*-bromomandelic acids. **3499**, Determination of $Cl^-$ in organic materials. **3532**, Determination of naphthalene-1:3:6-trisulphonic acid in plating soln. **3764**, Determination of lactose in casein. **3809**, Elementary organic analysis. **3810**, Determination of N. **3851**, Determination of org. compounds by chronopotentiometry.

## 4.—BIOCHEMISTRY
### INCLUDING DRUGS, FOOD, SANITATION, AGRICULTURE

#### Biological fluids, animal and vegetable tissues

3643. **Polarographic methods in clinical chemistry.** M. Březina (Polarographic Inst., Acad. of Sci., Prague). *Acta Chim. Acad. Sci. Hung.*, 1959, **18** (1–4), 69–78 (in German).—Various polarographic methods are discussed, and details are given for the determination of oxygen in blood, the determination of ketosteroids, and the use of the Brdička reaction. (*i*) *Oxygen in blood*—The basal soln. [0·004 *M* $K_3Fe(CN)_6$, 0·05 *M* KCl, 0·05 *M* $Na_2B_4O_7$, 0·1% of saponin and 0·1% of gelatin] is saturated with air, a sample is transferred to the polarographic cell and a layer of liquid paraffin is introduced. The soln. is polarographed from 0·0 V, *vs.* the AgCl electrode, and a known vol. of blood is added from a syringe, with precautions against contamination with air. The soln. is again polarographed after about 5 min. to allow the reaction to take place. A fresh soln. is prepared containing blood, but this time the soln. is aerated before polarographing. From these three results the oxygen content of the blood can be found. (*ii*) *Ketosteroi* —Progesterone is reduced at pH 6 to 7 in aq. ethar soln. when polarographed from −0·4 V, *vs.* t N.C.E. Deoxycorticosterone can be determined the presence of methyltestosterone at pH 9·5 50% aq. ethanol from −1·2 V, *vs.* the $Hg_2S$ electrode. The dimethylglycinehydrazone methyltestosterone can be polarographed at pH in aq. ethanol, from −1·4 V *vs.* the S.C.E. (*i The Brdička reaction*—This is used in the diagnos of certain diseases, and is based on the polarograph of the filtrate remaining after the pptn. of album from serum with sulphosalicylic acid. The cor pounds responsible for the reducibility of the filtra have been recognised, namely, a mucoprotein ar an albumin which is not pptd. by sulphosalicyl acid. H. M.

3644. **Infra-red spectra of some biochemic substances in water.** F. S. Parker (Dept. of Bi chem., State Univ. of New York, Brooklyn, U.S.A *Appl. Spectroscopy*, 1958, **12** (6), 163–166.—Infr red spectra in water can be obtained with the use a barium fluoride cell in conjunction with a tran mittance screen. The use of such spectra to show chemical change resulting from the dissolution an unstable compound is illustrated. The sol and solution spectra of α-oxoglutaric acid sho typically distinct differences. Spectra for organic acids, including those associated with t citric acid cycle, are given. K. A. PROCTOR

3645. **Determination of potassium in blood serur** A. E. Teeri and P. G. Sesin (Dept. of Agric. ar Biol. Chem., Univ. of New Hampshire, Durhar U.S.A.). *Amer. J. Clin. Path.*, 1958, **29** (1), 86–89.— A buffered 3% soln. of Na tetraphenylboron added to a suitably diluted protein-free sample serum and the K is determined by measuring th turbidity at 540 mμ. The method is rapid ar simple. Results are in good agreement with thos obtained by standard procedures. P. NICHOLLS

3646. **Complexometric determination of calciu in urine.** E. Knappe and V. Böckel (Dtsch. Akac d. Wissenschaft., Berlin). *Acta Chim. Acad. Sc Hung.*, 1959, **18** (1–4), 85–91 (in German).— Difficulties previously encountered in the determina tion of Ca in urine are attributed to the presence $SO^2_4{}^-$ which can be removed by passing the samp through a cation-exchange medium. The Ca together with the Mg, is adsorbed and can be re moved by washing with 7% HCl soln. The Ca i the eluate is titrated with EDTA soln., wit calcein as indicator. This is preferred to murexid or calcon since it gives a sharper end-point and mor accurate results. The recommended cation ex changer is Wofatit P, and the pH 2·5 to 3·0. Result are accurate to within ±0·34%. H. M.

3647. **Photometric determination of total calciu in serum and urine.** Yukio Ichinose (Nat. Inst. c Nutrition, Toyama-cho, Shinjuku-ku, Tokyo). *Agric. Chem. Soc. Japan*, 1958, **32** (9), 717–719.— Co-pptn. of $Mg^{2+}$ with calcium phosphate is avoide by pptn. of $Mg(OH)_2$ with NaOH. The ppt calcium phosphate must be washed thoroughly The P is determined photometrically at 780 m with ammonium molybdate and 1-amino-2-naph thol-4-sulphonic acid (**I**). *Procedure*—Mix th sample (0·2 ml) with 50% NaOH soln. (1 ml) and after 30 min., add $Na_2HPO_4$ soln. (5%) (0·5 m and aq. $NH_3$ soln. (28%) (4 ml). Set aside ove night and wash the ppt. four times with a mixtur

ethanol, *n*-pentanol, aq. $NH_3$ soln. (28%) and ater (40:3:20:40) containing $NH_4Cl$ (2·6 g per re); dissolve the ppt. in HCl (1:4) (0·5 ml), mix th $(NH_4)_2MoO_4$ soln. (2·5% in 5 *N* $H_2SO_4$) (0·5 ml) d **I** soln. (0·25%) (0·5 ml) and dilute to 10 ml for notometry. K. Saito

3648. **Direct flame-photometric determination of lcium in soil and plant extracts, water and serum th special reference to sodium, potassium and osphate interference.** M. Puffeles and N. E. essim (Div. of Chem. Anal., Min. of Agric., Telviv, Israel). *Anal. Chim. Acta*, 1959, **20** (1), 38–.—By using the EEL flame photometer for the termination of Ca, it was found that the presence Na in the sample caused a large positive error, a small positive error which became negative ith increasing concn., and phosphate a very large gative error. It was therefore concluded that it possible to determine Ca without prior separation oxalate in irrigation and drinking water, soil tracts and normal blood sera, but not in plant-h extracts and abnormal sera.

W. T. Carter

3649. **Determination of zinc and other elements in ants by atomic-absorption spectroscopy.** D. J. avid (Div. of Plant Industry, C.S.I.R.O., Canberra, .C.T., Australia). *Analyst*, 1958, **83**, 655–661.— mist of the sample soln. is introduced into a undegårdh air - acetylene flame placed between ie slit of a flat-field Hilger medium-quartz spectro-aph and a hollow-cathode discharge tube emitting termittent light of the element to be determined 50 cycles per sec. The plate holder of the ectrograph is replaced by a slit and photomulti-ier mounted in guide grooves to align the slit in ie focal plane of the spectrograph. This exit slit placed on the resonance line of the element to be termined, the transmitted light is picked up by ie photomultiplier and the amplified rectified gnal is measured with a millivoltmeter. The mplifier is adjusted to zero with the slit shutter osed and to full-scale deflection with the shutter pen and a mist of water entering the flame. The ercentage reduction in the reading when the water replaced by the sample soln. is a measure of the sorption by the flame of the resonance line of the ement. Results are given for Zn, Mg, Cu and Fe etermined in plant material. For Zn and Mg the ethod is as sensitive as other common methods and ss subject to interference from other elements. or Cu and Fe it is insufficiently sensitive in its resent form. A. O. Jones

3650. **Determination of traces of lead and bismuth organic material.** J. C. Gage (I.C.I. Ltd., Ind. ygiene Res. Lab., The Frythe, Welwyn, Herts., ngland). *Analyst*, 1958, **83**, 672–674.—It is shown at the method previously reported (*Ibid.*, 1955, , 789) for the determination of Pb in organic aterial is subject to interference by Bi. This n be avoided by reducing to 0·1 *N* the concn. of Cl used to extract Pb from its diethyldithiocarb-nate complex in organic soln. Experiments with hed spinach containing known amounts of Pb d Bi showed that each metal at a concn. of 1 p.m. in the fresh spinach can be determined with equate accuracy in the presence of 100 p.p.m. of e other. Lead and Bi together (each at a concn. 1 p.p.m.) can be determined in the same soln. by ccessive extraction with 0·1 *N* and 1·75 *N* HCl th recoveries within 10% of the expected values. Iron (10 p.p.m.) does not interfere with the determination of Bi, but causes slight reduction in the recovery of Pb. A. O. Jones

3651. **Three cases of acute lead poisoning. Analyses of organs for lead and observations on polarographic lead determinations.** O. Karlog and K. O. Møller (Copenhagen Univ., Denmark). *Acta Pharm. Tox., Kbh.*, 1958, **15** (1), 8–16.—After wet-oxidation of the tissue sample, Pb is extracted with dithizone at pH 7·5 in the presence of ammonium citrate, hydroxyammonium chloride, KCN and aq. $NH_3$. The dithizone is re-extracted with 2 *N* HCl, and Pb is determined polarographically. Calibration is rectilinear up to 200 $\mu$g of Pb per ml of final soln. Impurities in the dithizone do not interfere. Values obtained for various organs from three poisoning cases are given. W. H. C. Shaw

3652. **Colorimetric determination of inorganic phosphorus in the presence of glucose 1-phosphate and adenosine triphosphate.** Michinori Nakamura and Kenji Mori (Dept. of Agric. Chem., Univ. of Tokyo, Japan). *Nature*, 1958, **182**, 1441.—The method of Allen (*Biochem. J.*, 1940, **34**, 858) and its modifications have been investigated in respect of the hydrolysis of acid-labile phosphorus compounds during colour development. The amounts of 2:4-diaminophenol hydrochloride and reducing agent and the nature of the acid have some effect on the rate of hydrolysis, but the most important factor is the temp. If colour development is carried out at 18°, very little hydrolysis occurs.

H. F. W. Kirkpatrick

3653. **Determination of arsenic in biological material.** W. T. Oliver and H. S. Funnell (Dept. of Physiol. Sci., Ontario Vet. Coll., Guelph, Canada). *Anal. Chem.*, 1959, **31** (2), 259–260.—Heat the sample of macerated animal or plant tissue (1 g) with conc. HCl (15 ml) under reflux for 1 hr. Rinse the condenser with $H_2O$ (5 × 10 ml). Cool the combined macerate and rinsings to 25°, add 30% KI soln. (2 ml) and a 40% soln. of $SnCl_2$ in aq. HCl (3 drops), mix and set aside for 15 min. Add 0·1% Tween-80 soln. (1 ml), 2-ethylhexanol (7 or 8 drops) and zinc powder (5 g) and allow the vapours to pass in turn through layers of sand impregnated with Pb acetate, cellulose impregnated with $HgI_2$, and $HgI_2$ crystals. After 1 hr., elute the cellulose powder with 0·001 *N* iodine soln. containing 0·01% of sodium alginate (4 × 2 ml). To the eluate add 1% ammonium molybdate reagent (1 ml) and 0·15% hydrazine sulphate soln. (0·4 ml), mix and heat in boiling water for 10 min. Cool rapidly, dilute to 10 ml with $H_2O$, mix and measure the extinction at 720 m$\mu$ against a reagent blank. For samples that contain 20 to 50 $\mu$g of As, the coeff. of variation of results is $\simeq$2%; the recovery is almost quantitative. A. R. Rogers

3654. **Determination of iodine in marine algae and other plant materials.** R. Brühlmann (Kant. Lab., St. Gallen, Switzerland). *Mitt. Lebensmitt. Hyg., Bern*, 1959, **50** (1), 14–17.—The sample is mixed to a paste with $K_2CO_3$ and water and is then dried and carbonised at 500°. The iodine is extracted, as iodide, from the residue with hot water. Acidified $CHCl_3$ is added followed by $NaNO_2$ to oxidise the $I^-$ to iodine, which is extracted into the $CHCl_3$. The extinction of this soln. is measured at 510 m$\mu$ or with suitable colour filters. The accuracy is $\simeq \pm 0{\cdot}05$ mg absolute in the concn. range of 2·5 to 10 mg of iodine. G. P. Cook

3655. **Simple analytical method to determine the proportions of mother and daughter substance in radioactive preparations.** A. Catsch (Inst. für Strahlenbiol. a. d. Reaktor-Sta., Karlsruhe, Germany). *Experientia*, 1958, **14** (9), 345–346 (in German).—A simple and time-saving numerical method is described which permits the rapid determination of mother-to-daughter ratios in biological specimens containing radio-isotopes.
P. Nicholls

3656. **Comparison of the results obtained from application of the Hint - Thorsen and anthrone methods for the determination of dextran in blood.** H. Szafranowa, I. Michalska, A. Nowicka and I. Nykowski (Dept. of Pharmacol., Inst. of Pharm., Warsaw). *Acta Polon. Pharm.*, 1959, **16** (1), 35–43.—From results of determinations by both methods, it was found that there was a statistically significant discrepancy. It is concluded that the Hint - Thorsen method (*Acta Chem. Scand.*, 1947, **1**, 808), slightly modified, is more suitable for control determinations of dextran in blood, as it proved to be simpler and easier, and gave more consistent results, than the anthrone method.
W. B. Miaskowski

3657. **Quantitative colorimetric determination of colchicine in aqueous solution, and studies on its application to urine.** E. M. Pearle (Arthritis Clinic, 4th Div. Bellevue Hospital, New York Univ., U.S.A.). *J. Chromatography*, 1959, **2** (1), 108–113.—An attempt to determine colchicine in urine by extraction with 1:2-dichloroethane followed by paper chromatography with benzene - formamide (Burton *et al.*, *J. Biol. Chem.*, 1951, **188**, 763) gave very low recovery although the method was successful with aq. soln. of colchicine.
G. Burger

3658. **Binding affinity of purified plasma proteins for phenylethylbiguanide, an oral hypoglycaemic compound.** H. G. Shepherd, jun., and H. J. McDonald (Dept. of Chem., Grad. Sch., Loyola Univ., Chicago, Ill., U.S.A.). *Clin. Chem.*, 1958, **4** (6), 496–509.—The colorimetric method described for the determination of phenylethylbiguanide is based on the method of Rosenberg *et al.* for the determination of arginine (*Biochem. J.*, 1956, **63**, 153).
H. F. W. Kirkpatrick

3659. **Modification of Malkin's screening test for the detection of artifactually high organic iodine compounds in sera.** M. Barker and E. B. Man (Yale Univ. Med. Sch., New Haven, Conn., U.S.A.). *J. Lab. Clin. Med.*, 1958, **52** (4), 659–660.—Improved sensitivity in the test (*cf.* Malkin, *Anal. Abstr.*, 1957, **4**, 223) is attained by substituting 0·5 ml of aq. KI soln. (1·4 mg in 100 ml) for 0·5 ml of water. The addition of 2 drops of 27 *N* $H_2SO_4$ after the digestion with KOH enables the ceric and arsenite reagents for the butanol-extractable iodine test to be used for both tests.
W. H. C. Shaw

3660. **Spectrophotometric method for the determination of Evans blue dye in the presence of haemolysis and turbidity.** L. H. Hamilton (Marquette Univ. Med. Sch., Milwaukee, Wis., U.S.A.). *J. Lab. Clin. Med.*, 1958, **52** (5), 762–767.—Interference in the determination of Evans blue (azovan blue) in plasma by haemoglobin with or without additional turbidity (fat) may be eliminated by the method described. With the spectrophotometer used, the equation $E_{625}$ (corr.) = $E_{625}$ (obs.) — 1·793 $E_{745}$ was found to be correct within an E value of 0·003 for 22 determinations in plasma or serum samples with interference of the two types.
W. H. C. Shaw

3661. **Simple rapid and accurate method of extracting T-1824 [azovan blue] from plasma adapted to the routine measurement of blood volume.** T. J. Campbell, B. Frohman and E. B. Reeve (Colorado Univ. Med. Sch., Denver, U.S.A.). *J. Lab. Clin. Med.*, 1958, **52** (5), 768–777.—In the method described, the dye is displaced from combination with albumin in the sample with Teepol in phosphate soln. The mixture is then passed through a column of wood cellulose (Solka Floc SW-40-A) on which the dye is adsorbed and interfering substances are eluted with 2% aq. $Na_2HPO_4$ soln. The dye is then eluted with acetone - water (1:1) adjusted to pH 8·0 with *N* NaOH, and the extinction is measured at 615 mμ after adjustment of the pH to 6·8 with $KH_2PO_4$. The observed results may be related to "normal" blood volume by the nomogram given.
W. H. C. Shaw

3662. **Micro-determination of acetone in biological fluids.** M. U. Tsao, G. H. Lowrey and E. J. Graham (Dept. of Pediatrics and Communicable Diseases, Univ. of Michigan Med. Sch., Ann Arbor, U.S.A.). *Anal. Chem.*, 1959, **31** (2), 311–314.—Heat 2:4-dinitrophenylhydrazine (10 mg) with a mixture of conc. $H_2SO_4$ (0·05 ml) and 95% ethanol (10 ml) at 50° until most has dissolved, and cool. Pipette 150 μl of this soln. into an absorptiometer tube, the lower part of which is immersed in ice water and the upper part maintained at about 38°, Place a 10-μl aliquot of the sample on filter-paper (8 mm × 16 mm) supported within the tube and allow diffusion to proceed for 90 min. Remove the tube, and after a further 30 min. at room temp. add 9 *N* NaOH (0·3 ml). Mix and set aside for 30 min. Add 50% ethanol (3 ml) and measure the extinction at 540 mμ, 15 min. after the addition of the alcohol. A correction may be applied for interference caused by acetaldehyde. The limits of error ($P = 0·95$) for the recovery of 5 μg of acetone from samples of blood and urine are 1·5% and 1·2%, respectively.
A. R. Rogers

3663. **Enzymatic method for glucose determination in body fluids.** E. F. Beach and J. J. Turner (Biochem. Lab., Met. Life Ins. Co., New York, U.S.A.). *Clin. Chem.*, 1958, **4** (6), 462–475.—Glucose oxidase - peroxidase from horseradish root (preparation described), and *o*-anisidine as colour reagent, are used in the method described, which is applied to the qual. detection of glucose in urine, and its quant. determination in urine and blood.
H. F. W. Kirkpatrick

3664. **Reaction between *meso*inositol and uranyl acetate.** P. Meredith and H. G. Sammons (Dept. of Med. Biochem. and Pharmacol., Univ., Birmingham, England). *Analyst*, 1958, **83**, 686.—A reaction between *meso*inositol and uranyl acetate soln. may serve as a method of detection of *meso*-inositol on paper chromatograms and of its determination in soln. after chromatographic separation of other polyols. The chromatogram is lightly sprayed with a 2% aq. soln. of uranyl acetate and is immediately examined under u.v. light. A green fluorescence indicates the presence of inositol. In aq. soln. (pH 4·4) the large blank fluorescence of uranyl acetate is only feebly enhanced by inositol. When increasing amounts of NaOH are added, the

ease in fluorescence caused by inositol is de-
sed to the point where the effect of inositol is
ersed and quenching occurs, and this quenching
ct, being greater than the enhancement, is more
able for measurement. A tentative method is
cribed in which the quenching effect is used for
determination of inositol eluted from paper
omatograms. Standard graphs are reproducible
he range 20 to 200 μg. The absorption graph
the yellow complex formed by inositol and
nyl acetate has peaks at 356, 315 and 240 mμ,
the sensitivity attained does not approach that
he quenching method. A. O. JONES

665. **Biochemical aspects of bovine ketosis. cro-determination of pyruvate, citrate, α-oxo-arate and succinate.**] S. J. Bach and K. G. bitt (Dept. of Physiol., Univ. of Bristol, Eng-d). *Biochem. J.*, 1959, **72** (1), 87–92.—Standard ro-methods are adapted for the determination of o 2 μg of pyruvate, citrate and α-oxoglutarate serum, and a new method is described for the ermination of succinic acid. Pyruvate and xoglutarate are determined by modifications of dinitrophenylhydrazone method, and citrate the pentabromoacetone method. Succinic acid xtracted with diethyl ether from serum deprotein-with tungstic acid. After evaporation of the er, the residue is dissolved in phosphate buffer, 7·6, and the enzymic (succinoxidase) reduction cytochrome *C* by succinic acid in the presence absence of malonate is determined spectro-otometrically at 550 mμ. J. N. ASHLEY

666. **Chromatographic separation of pyruvic, lacetic and α-oxoglutaric acid from tissue tures.** G. A. Abdel-Tawab, E. Broda and G. lner (Univ., Vienna). *J. Chromatography*, 1959, ), 99–107.—These acids have been separated by cending chromatography of their 2:4-dinitro-nylhydrazones on filter-paper freshly impreg-ed with 0·1 *M* phosphate buffer (pH 7·4), with utanol - 3% aq. $NH_3$ (1:1) as solvent. The uvic acid derivative gives two spots when the l is extracted from a tissue culture, and the ivatives of oxalacetic and α-oxoglutaric acids one h. The oxalacetic acid derivative is decomposed he pyruvic acid derivative by moderate heat, so t exposure to heat during analysis should be ided. The bands were extracted with buffer n. and the concn. determined colorimetrically. this analysis formed part of an investigation with io-tracers, the activity of the bands was deter-ed with a $CO_2$-filled Geiger counter. The deriv-es were formed in the deproteinised culture dium and extracted with ether; 2 μg of the acids be determined. G. BURGER

667. **Formation of indol-3-ylacetic acid and otamine in animals. Method for estimation of ol-3-ylacetic acid in tissues.** H. Weissbach, King, A. Sjoerdsma and S. Udenfriend (Lab. of . Biochem., Nat. Heart Inst., Bethesda, Md., .A.). *J. Biol. Chem.*, 1959, **234** (1), 81–86.—ensitive and specific method is described for the ermination of indol-3-ylacetic acid (**I**) in urine tissues. It is based on a modified xanthhydrol tion as described for the determination of otophan by Dickman and Crockett (*Anal. Abstr.*, 3, **3**, 3721). The urine is extracted with aq. - $CHCl_3$, and the $CHCl_3$ layer is extracted with sphate buffer (pH 7·0). An aliquot of the buffer is treated with HCl, xanthhydrol and $NaHSO_3$ after 5 to 10 min. the extinction of the pink colour is measured spectrophotometrically at 520 mμ. For 8 to 200 μg of **I**, the extinction is proportional to concn. With extracts of tissues, increased sensitivity is needed, and this is obtained by a fluorimetric assay after pptn. of proteins.
J. N. ASHLEY

3668. **Concentration of vitamin $B_{12}$ from urine by adsorption on carbon.** C. H. Buchholz (Veterans Admin. Hosp., Long Beach, Calif., U.S.A.). *J. Lab. Clin. Med.*, 1958, **52** (4), 653–656.—Increased sensitivity in the assay of radio-cyanocobalamin is attained by adsorption from the acidified sample on to activated carbon, which is then counted in a well-type scintillation counter. By this method a Schilling test may be carried out with a test dose of 0·05 μC. W. H. C. SHAW

3669. **Determination of bilirubin in serum as alkaline "azobilirubin".** J. Fog (Med. Dept. B, Univ. Clinic, Oslo City Hospital, Norway). *Scand. J. Clin. Lab. Invest.*, 1958, **10** (3), 241–245.—The method of Jendrassik and Gróf (*Biochem. Z.*, 1938, **297**, 81) is adapted for use with a spectrophotometer. The van den Bergh reaction with diazotised sulphanilic acid is carried out on 1 ml of serum in the presence of caffeine - sodium benzoate accelerator. After making the soln. alkaline, the absorption is measured at 600 mμ. At this wavelength the absorption of the yellow non-bilirubin pigments of serum, and of pigments preformed or arising in the reaction, is negligible. Beer's law is obeyed over a wide range of bilirubin concn., and the method is specific and accurate.
D. W. Moss

3670. **Paper-chromatographic separation of the coproporphyrin isomers I and III.** L. Eriksen (Inst. Med. Biochem. and Physiol., Univ., Oslo, Norway). *Scand. J. Clin. Lab. Invest.*, 1958, **10** (3), 319–321.—The separation is performed by a modification of an earlier column method (*Ibid.*, 1957, **9**, 97), which depends on the number of acid groups in the porphyrin molecule. The mixture of compounds is dissolved in 10% aq. $NH_3$ - acetone (3:10), and is spotted on Whatman No. 1 paper, which is then developed by ascending chromatography with 2:6-lutidine - water in an atmosphere of ammonia. No temp. control is necessary, but light should be excluded. The method is simple and reliable. D. B. PALMER

3671. **Accumulation of acetylmethylcarbinol and acetylethylcarbinol by a mutant of *Neurospora crassa* and its significance in the biosynthesis of *iso*leucine and valine. [Determination of acetylmethylcarbinol and acetylethylcarbinol.]** R. P. Wagner, A. Bergquist and H. S. Forrest (Genetics Lab., Dept. of Zool., Univ. of Texas, Austin, U.S.A.). *J. Biol. Chem.*, 1959, **234** (1), 99–104.—The method is based on the condensation of each carbinol with 2:4:5-triamino-6-hydroxypyrimidine to give the corresponding pteridines. The condensation products are dissolved in 1% aq. $NH_3$ and chromatographed on paper in 1% aq. $NH_3$ in *n*-propanol. The two fluorescent bands are cut out, the material from each is eluted with 1% aq. $NH_3$, and the amounts of each pteridine are ascertained from the extinctions at 355 mμ of each eluate in 0·1 *N* NaOH.
J. N. ASHLEY

3672. **Chromatographic identification and determination of xylose and arabinose in the pentosans of soya bean.** A. Troparevsky, A. E. A. Mitta and

M. L. Pisarello (Dept. of Biol. Chem., Univ., Buenos Aires). *An. Asoc. Quím. Argentina*, 1958, **46** (3), 253–257.—The xylose and arabinose contents of soya bean (variety CNS 24 from S. Carolina), determined colorimetrically after paper-chromatographic separation of the sugars, were 0·35% and 3%, respectively; 0·91% of another pentose, presumably ribose, was also present. Satisfactory separation of both xylose and arabinose from hexose sugars was not obtained on the same chromatogram and, for the determination, xylose was separated by using ethyl acetate - pyridine - water - acetone (2:1:1:1), and arabinose by using phenol - water. An extract of the defatted soya bean was prepared by heating under reflux for 1 hr. with 6·5 ml of HCl ($d$ = 1·125) and 65 ml of water, defecating with 15 ml of 10% $Na_2WO_4$ and diluting to 100 ml. For the elimination of salts, a 5-ml aliquot was evaporated to dryness on the water bath, treated with 5 ml of dry pyridine at 100° for 10 min., cooled and filtered. The pyridine soln. was evaporated at <40° and the residue dissolved in 2·5 ml of water. The sugars were separated by ascending chromatography on Whatman No. 1 paper, eluted, and determined colorimetrically by the method of Dubois (*Nature*, 1951, **168**, 167). E. C. Apling

3673. **Detection of pollen flavonoids by fluorescence on impregnated papers.** G. E. Inglett, R. R. Miller and J. P. Lodge (Dept. of Health, Educ. and Welfare, Public Health Service, R. A. Taft San. Engng Center, Cincinnati, Ohio, U.S.A.). *Mikrochim. Acta*, 1959, (1), 95–100 (in English).—Strips are prepared by dipping Whatman No. 4 paper into 0·1% aq. soln. of $ZrOCl_2.8H_2O$, $AlCl_3.6H_2O$ or $BeSO_4$ (this soln. adjusted to pH 11), and allowing to dry in air. Many flavonoid glycosides and related compounds, applied as 0·01% ethanolic soln. and allowed to dry in air, form chelate compounds which fluoresce under u.v. light. In many cases the colour and intensity of the fluorescence differs according to the strip, permitting qual. identification. Results are presented for 34 substances and it is shown that orchard-grass pollen-extract contains dactylin and *iso*quercetin, while timothy-grass pollen-extract contains only dactylin. Limits of identification are listed for 21 compounds giving an observable spot. T. R. Andrew

3674. **Specific colour reaction for rutin.** Shozo Kamiya (Nat. Hygienic Lab., Tamagawa-yoga, Setagaya-ku, Tokyo). *Japan Analyst*, 1958, **7** (11), 717–718.—On application of the modified indophenol method for the detection of phenols (Itai and Kamiya, *Anal. Abstr.*, 1959, **6**, 3590), rutin (>2 μg) changes at first to blue then to green. The colour fades on the addition of NaClO (0·02% aq. soln., 2 drops). Among related compounds, hesperidin (>10 μg), hesperetin (>2 μg) and acacetin (>5 μg) give a similar coloration which becomes more intense on addition of NaClO.

K. Saito

3675. **Method for determining monosaccharides and uronic acids in wood hydrolysates.** O. Perilä and T. Seppä (Lab. of Wood Chem., Inst. of Technol., Helsinki, Finland). *Suomen Kem., B*, 1958, **31** (12), 383–384.—This method makes it possible to determine monosaccharides and uronic acids by paper chromatography without previous fractionation of the components by other methods. After total hydrolysis of the wood with $H_2SO_4$ soln. the resulting sugar soln. is neutralised with $BaCO_3$, filtered, and concentrated. Whatman No. 1 paper saturated with 0·05 $N$ $Ba(OH)_2$ is employed. Whe using neutral solvents, *e.g.*, ethyl methyl ketone acetone - water (15:5:3), the monosaccharides a separated in the normal manner, but the uron acids move only a short distance. The monosacch arides are determined by the method of Matzusa and Ward (*TAPPI*, 1957, **40**, 650). When th uronic acids are also to be determined, only or edge of the paper, used as a stationary phase, treated with $Ba(OH)_2$ soln. After elution with neutral solvent as described above, the paper str is dried, and the uronic acids are separated in th crosswise direction with an acid solvent, *e.g* ethyl acetate - acetic acid - formic acid - wat (18:3:1:4). E. Sjöström

3676. **Studies on tannins. VII. Colorimetr determination of (+)-catechin in catechu.** Koi Kimura, Yukishige Satomi and Shigeaki Kuwan (Pharm. Fac., Osaka Univ., Hotarugaike, Toyo naka). *J. Pharm. Soc. Japan*, 1958, **78** (4), 325 329.—The colorimetric method of Mayer for th determination of (+)-catechin (**I**) with vanillin i HCl (*Leder*, 1956, **7**, 33) was applied, with som modifications, to the analysis of Gambier catechu For the paper-chromatographic separation of from Gambier tannin (**II**), a mixture of benzen propanol, acetic acid and water (4:2:1:1, by vol is preferred ($R_F$ for **I**, 0·25; for **II**, ≃0). Th sample (1 g) is extracted with methanol in Soxhlet apparatus, the extract is diluted to 50 m and one drop is chromatographed. The spot of is cut out, dried *in vacuo* at 90° for 6 hr., extracte with methanol (2 ml), mixed with vanillin in meth anolic HCl (3 vol. of 10% vanillin in methanol an 1 vol. of 35% HCl) (5 ml) and the extinction measured at 500 mμ after 15 min. K. Saito

3677. **Studies on wasabi. IV. Determination sinigrin.** Zenji Nagashima, Masaaki Uchiyama an Yasushi Utsugi (Fac. of Agric., Shizuoka Univ Mishima). *J. Agric. Chem. Soc. Japan*, 1958, **3** (7), 521–525.—Sinigrin (**I**) is separated wit Amberlite LR-4B (Cl), with 0·2% KOH soln. a eluting agent (Nagashima, *Ibid.*, 1957, **31**, 514), an is then determined by its quant. reduction $K_3Fe(CN)_6$ in alkaline soln. *Procedure*—Crus wasabi root (0·5 g) with methanol (70%, 5 ml) an sand, dilute with methanol (70%, 10 ml) an centrifuge. Repeat the extraction. Pass a 5-m portion of the methanolic soln. through a colum of resin (diam., 6 mm; vol. of resin, 0·7 ml; rate flow, 0·1 ml per min.), wash with water (40 ml) an elute **I** with 0·2% KOH soln. (0·2 ml per min., 5 ml). Heat a 5-ml portion of the eluate with a $K_3Fe(CN)_6$ soln. (1·650 g per litre containing 10·6 of $Na_2CO_3$) (2 ml) in a water bath for 15 min. an titrate the excess of $K_3Fe(CN)_6$ soln. iodimetrically K. Saito

3678. **Electrophoretic analysis of plant-virus prep arations.** P. M. Townsley (Chem. Div., Canad Dept. of Agric., Vancouver, B.C.). *Canad. Biochem. Physiol.*, 1959, **37** (1), 119–126.—Tr (hydroxymethyl)methylamine maleate buffer (p 7·0), with 0·7% agar and a final buffer molarity 0·02, is used. Leaf juice is expressed at 0° an applied immediately to the origin. Electrophores is carried out with a p.d. of 150 V and a current 14 mA. The location of tomato mosaic virus ar potato virus X is effected by autoradiograph serological and protein-staining methods.

H. F. W. Kirkpatrick

679. **Paper-chromatographic determination of tine phosphate and orthophosphate in tissue acts.** E. Gerlach and J. Janke (Inst. of Physiol., v. of Freiburg). *Biochem. Z.*, 1958, **330** (7), –575.—A new solvent system is described for use he two-dimensional chromatographic separation reatine phosphate (**I**) and orthophosphate (**II**) n each other and from other phosphorus com- nds. This solvent consists of methanol - ropyl alcohol - 25% aq. $NH_3$ - $H_2O$ (9:6:3:2), ch is used for the first run, followed by di*iso*- pyl ether - *n*-butanol - formic acid (98%) (4:3:2). e method used is that of Gerlach *et al.* (*Naunyn-miedebergs' Arch. exp. Path. Pharmak.*, 1955, , 9). The $R_F$ values of 28 phosphorus-containing npounds are given, that of **I** being 1·00, and that II being 0·52. Recoveries of 96·5% to 99·5% e obtained. This new solvent is applied to the ermination of **I** and **II** in various rat organs and ues. The organs and tissues are frozen *in situ*, oved, and extracted with ice-cold $HClO_4$. erfering ions are removed by treating the extract h a soln. of EDTA. Following neutralisation of soln. and removal of the pptd. $KClO_4$, aliquots taken for chromatography. The developed omatogram is sprayed with a molybdate reagent, l the revealed phosphorus compounds are deter- ned by the method of Berenblum and Chain *ochem. J.*, 1938, **32**, 295). Results are reported the content of **I** and **II** of skeletal muscle, heart scle, brain, intestinal mucosa, kidney and liver, l the levels quoted are affected significantly by technique of tissue isolation. The possibility sing this method in studies with $^{32}P$ is discussed.

D. B. Palmer

680. **Paper-chromatographic determination of atine phosphate.** B. E. Wahler (Arbeitsstelle f. eislaufforsch. der Dtsch. Akad. der Wissen- aften zu Berlin, Arbeitsgruppe f. Biochem., rlin-Buch). *Naturwissenschaften*, 1959, **46** (1), —A quant. determination of orthophosphate l creatine phosphate or phosphoglycocyamine in presence of each other is obtained by the paper omatography of a weakly acid extract (pH 5 7). Data are tabulated of $R_F$ values and identi- ng reactions for the constituents of heart and in muscle. A special procedure is described for determination of molybdate-labile N-phosphono ds.

J. L. Prosser

681. **Identification of histamine, N-dimethylhist- ine, N-acetylhistamine and acetylcholine in *Spin- a oleracea*.** W. Appel and E. Werle (Wissen- aft. Lab. der Chirurg. Klinik, Univ., München). *neimittel-Forsch.*, 1959, **9** (1), 22–26.—Extracts spinach were prepared with the following reagents nethanol, water, 0·1 *N* HCl and basic Pb tate soln. Each extract was subjected to ion- hange chromatography. The iminazole deriv- ves contained in individual fractions were mined and identified by paper chromatography l tested pharmacologically by studying their ct on the blood pressure of dogs. The main nazole derivatives were histamine and N- tylhistamine. The presence of the latter was pected when much acetylcholine was found. all amounts of dimethyl- and traces of trimethyl- amine were also present. In addition to paper- omatographic and pharmacological studies of ious components, total iminazole derivatives were ermined by the diazo reaction.

M. H. Sawistowska

3682. **Colour tests and determination of noradrenalone hydrochloride in non-aqueous medium in the presence of adrenalone hydrochloride.** I. Gyenes, A. Mizsei and L. Szagó (Anal. Dept., Gedeon Richter A.-G., Budapest, Hungary). *Acta Chim. Acad. Sci. Hung.*, 1958, **16** (4), 389–402 (in English).—A satisfactory quant. test is described. Dissolve 93 to 97 mg of sample in pure pyridine and dilute the soln. to 50 ml with solvent. To 1 ml add 5 ml of reagent [4% (w/v) $HgCl_2$ in pyridine], shake, stopper the tube and set aside for 1 hr. at 25°. Measure the extinction at 353 m$\mu$ in a 1-cm cell. This test will detect 0·003 to 0·03 mg of noradrenalone hydrochloride (**I**) in the presence of 2 mg of adrenalone hydrochloride (**II**). A qual. test consists in adding 4% (w/v) Pb acetate trihydrate in dimethylformamide (5 ml) to a soln. of 10 mg of **I** in the same solvent (1 ml), when the presence of 0·02 mg of **II** is shown by the formation of a ppt. with a distinct greenish-blue tint.

H. F. W. Kirkpatrick

3683. **Determination of uridine and thymine in small samples of nucleic acid protein residue.** K. F. Jervell, C. R. Diniz and G. C. Mueller (Wisconsin Univ. Med. Sch., Madison, U.S.A.). *Arch. Biochem. Biophys.*, 1958, **78** (1), 157–164.—The sample is hydrolysed under controlled conditions with 98% formic acid, and the hydrolysate is then purified by passage through a column of prepared Dowex ion-exchange resins. The first fraction obtained with 0·01 *N* HCl contains uridine, uracil and thymine which, after evaporation of the HCl, are chromatographed by the descending technique on Whatman No. 52 paper with water-saturated *n*-butanol. After development, appropriate areas, identified under u.v. light, are cut out and eluted with 0·01 *N* HCl, and individual compounds are then determined from the extinctions of the eluates. The procedure is applicable to isotopically labelled nucleic acids.

W. H. C. Shaw

3684. **Quantitative determination of xanthurenic acid in urine.** R. H. H. Richter (Frauenklinik, Univ., Bern, Switzerland). *Chimia*, 1958, **12** (11), 328.—To assure quant. recovery of xanthurenic acid (100 to 500 $\mu$g) from urine (4 ml) with $(NH_4)_2SO_4.Fe_2(SO_4)_3$ reagent, it is essential to run recovery checks, since some literature procedures give variable recoveries. Citric acid, salicylic acid, ascorbic acid and EDTA interfere. The urine must be at pH 6 to 8 before the addition of buffer, and should be sampled when subjects are not receiving medication.

J. P. Stern

3685. **Isolation, detection and measurement of microgram quantities of labelled tissue nucleotides.** K. K. Tsuboi and T. D. Price (Cornell Univ. Med. Coll., New York, U.S.A.). *Arch. Biochem. Biophys.*, 1959, **81** (1), 223–237.—The preliminary separation of labelled nucleotide mixtures, obtained from tissue samples after the administration of $^{32}P$, from non-nucleotide activity is attained by adsorption on activated charcoal (Norit A). After separation and washing, the nucleotides are eluted from the charcoal and individual components are then separated by two-dimensional paper chromatography. The compounds are located by radioautography and by photography under u.v. light. The reactions of Norit A with purine and pyrimidine compounds in general, their chromatographic behaviour with different solvent systems, and the identification and specific activity of the isolated nucleotides of rat organs are discussed.

W. H. C. Shaw

3686. **Estimation of pentose- and deoxypentose-nucleic acids in ox liver.** S. K. Dutta (Bengal Immunity Res. Inst., Calcutta). *Indian J. Pharm.*, 1959, **21** (1), 8–12.—To separate pentosenucleic acid (**I**) and deoxypentosenucleic acid (**II**) from the mixture of nucleic acids, the method of Dutta *et al.* (*cf. Brit. Abstr. C*, 1953, 359) is used. By hydrolysis of the isolated **I** and **II** with 60% $HClO_4$ at 100° for 1 hr., and chromatography of an aliquot of the neutralised hydrolysate with *n*-butanol - pyridine - water (6:4:3), separation of the constituent purines and pyrimidines is obtained. These are determined spectrophotometrically after location by u.v. photography (Markham and Smith, *Biochem. J.*, 1949, **45**, 294), and elution with 0·1 *N* HCl at 37° for 16 hr. A further aliquot of the hydrolysate is analysed for N and P by a micro-method (Jones *et al.*, *J. Chem. Soc.*, 1951, 623). The number of moles of the bases per 100 g-atoms of P can then be calculated, and by determining the molar concn. of uracil and thymine per 100 g-atoms of P the amounts of **I** and **II** originally present can be calculated. For the determination of **I** and **II** in ox liver, the samples are homogenised, treated with ice-cold 1% $HClO_4$, and the ppt. is washed with 0·5% $HClO_4$, ethanol, and diethyl ether. The dry material is then extracted twice with 6% $HClO_4$ at 80° for 30 min., the extracts are combined, and concentrated at 100° for 60 min. After neutralisation, the soln. is passed through a column of Zeo-Karb 215 (hydrogen form), then through a column of Decolorite, and the percolate is concentrated and analysed chromatographically as previously described. From the uracil and thymine content the original amounts of **I** and **II** are calculated. Results obtained by this method are compared with those from two other methods which are based on (*i*) determination of P, and (*ii*) determination of the sugar moiety. With pure **I** and **II** the results from the present method agree only with those by method (*ii*), but with samples of ox liver the results by all 3 methods differed. Possible reasons for this are discussed. D. B. Palmer

3687. **Gas-chromatographic investigation of the nitrometer gases resulting from Van Slyke amino-group determinations.** G. Kainz and H. Huber (II Chem. Inst., Univ., Vienna). *Mikrochim. Acta*, 1959, (1), 51–60.—Thirty-seven organic compounds, including many that have been observed to give high values for amino nitrogen, have been treated by the Van Slyke method and the nitrometer gases examined by gas chromatography. With the exception of uric acid, which yielded pure N, all the compounds studied gave mixtures of N and $N_2O$ in proportions which were affected by substituents. It is suggested that the presence of $N_2O$ is indicative of anomalous high values. T. R. Andrew

3688. **Qualitative aldehyde reactions. Identification of amino acids.** R. W. Storherr (Georgia Exp. Station, Experiment, U.S.A.). *Anal. Chem.*, 1959, **31** (2), 268–270.—Reactions between aldehydes and amino acids in glacial acetic acid provide a new means for the identification of specific amino acids. Furfuraldehyde reacts with most common amino acids producing a common absorbance maximum in the range 360 to 380 mμ. The lysines and ornithine exhibit a second peak at 515 to 530 mμ which is specific for this group of diamino acids. *sym.*-Trioxan reacts specifically with hydroxyproline giving a maximum at 492 to 494 mμ. Only milligram amounts of original protein are required for the identifications. G. P. Cook

3689. **Chromatography of dipolar ions. Activit coefficients of amino acids and peptides in ion exchange resins.** J. Feitelson (Hebrew Univ Jerusalem, Israel). *Arch. Biochem. Biophys* 1959, **79**, 177–186.—A study is made of the distribu tion of glycine, alanine and leucine and their simpl peptides on Dowex-50 ion-exchange resin (4% cross linked) at different pH values of eluent buffer an constant $Na^+$ concn. The equilibria involved i chromatography, the distribution and activit coefficients and the factors governing resin - solut interaction are discussed. W. H. C. Shaw

3690. **Rapid paper-chromatographic procedur for the quantitative determination of hydroxyproline** H. R. Roberts, M. G. Kolor and W. Bucek (Nat Dairy Products Corp., Oakdale, Long Island, N.Y U.S.A.). *Nature*, 1958, **182**, 1602.—Modification c a previously described method (Roberts and Kolo *Nature*, 1958, **181**, 837) reduces the time of develop ment from 40 hr. to 4 hr. Horizontal chromato graphy replaces descending chromatography an development at a higher temp. is carried out in a oven at 60°. H. F. W. Kirkpatrick

3691. **The Sakaguchi reaction of arginine o filter-paper.** K. R. Bhattacharya, J. Datta an D. K. Roy (Indian Inst. for Biochem., Calcutta) *Arch. Biochem. Biophys.*, 1958, **77** (2), 297–311.— The effects of different concn. of 1-naphthol arginine, hypobromite, urea and alkali, and c temp., on the colour developed in the reaction ar studied. The mechanism of the reaction is dis cussed in relation to the results obtained, and procedure for the determination of arginine o paper chromatograms is given. W. H. C. Shaw

3692. **Spectrophotometric determination of argi nine by the Sakaguchi reaction.** Kazuo Satake an J. M. Luck (Dept. of Chem., Stanford Univ., Calif U.S.A.). *Bull. Soc. Chim. Biol.*, 1958, **40** (12) 1743–1756 (in English).—A method similar to that o Szilágyi and Szabó (*cf. Anal. Abstr.*, 1958, **5**, 3122) but with 8-hydroxyquinoline instead of 1-naphthol is described. The test soln. (1 to 25 μg of arginin per ml) (2 ml) is mixed with 2 ml of 0·02% 8 hydroxyquinoline in 3 *N* NaOH, followed by 1 m of 0·1% N-bromosuccinimide, added with shaking After 5 to 30 min. the extinction is read at 500 m against water as blank. Hydrolysates containin inhibitory concn. of other amino acids are dinitro phenylated by the method of Porter and Sange (*Biochem. J.*, 1948, **42**, 287), and interfering amin acids are removed by extraction with diethyl ethe Dinitrophenol arginine in 0·1 *N* HCl is used as standard. Alternatively, untreated hydrolysate ma be determined, with 1 ml of hydrolysate plus 1 m of standard arginine soln. as a working standard. D. G. Moss

3693. **New colour reaction for tryptophan c tryptophan-containing proteins.** R. L. Searc (Los Angeles County Osteopathic Hosp., Calif U.S.A.). *Arch. Biochem. Biophys.*, 1959, **81** (1 275–276.—The method is based on the developmen of a purple colour when tryptophan, or protein containing it, are treated with toluene-*p*-sulphoni acid. Calibration is rectilinear with up to 4·0 m of serum of known globulin concn., serum tota globulins or serum γ-globulins. *Procedure*—T 0·1 to 4·0 mg of protein fractions add 10·0 ml c 12% toluene-*p*-sulphonic acid in glacial acetic acid Heat at 100° for 15 min., cool and read the extinc tion against a reagent blank at 560 mμ. W. H. C. Shaw

694. **Methods for the qualitative, semi-quantitative and quantitative determination of iodoamino s and of inorganic iodide in iodoprotein digests in human serum.** R. H. Mandl and R. J. k (Boyce Thompson Inst. Inc., Yonkers, ., U.S.A.). *Arch. Biochem. Biophys.*, 1959, **81** 25–35.—The method described is suitable for m and iodoprotein digests obtained after the inistration of $^{127}I$. After incubation with reatin, the iodoamino acids are concentrated extraction into *n*-butanol and then submitted chromatography on cellulose powder and loped with *iso*butyl alcohol - 3% w/v aq. $NH_3$ ). This treatment separates thyroxine, 3:5:3′-odothyronine and other iodothyronines from o- and di-iodotyrosine, $I^-$, and other amino s. The two fractions are concentrated, and re-chromatographed on Whatman No. 3 paper the descending technique for 24 hr. with the ve solvent. The concn. of the compounds may stimated visually by comparison with known dards after treatment with a $Ce(SO_4)_2$ - arsenite gent, followed by counter-staining with methyl- blue (sensitivity 0·1 $\mu$g of organic iodine). quant. purposes the spots are cut out and ed, and the compounds determined with the c - arsenite reagent either visually or, for im- ved reproducibility, with a recording colorimeter sitivity 0·005 $\mu$g of organic iodine). Dis- ancies between results for thyroxine and bio- cal activity are discussed. W. H. C. Shaw

695. **Zone electrophoresis of cerebrospinal fluid tarch gel.** J. H. Pert and H. Kutt (Neurolog. vice, Bellevue Hosp., Cornell Univ. Med. Coll., ., U.S.A.). *Proc. Soc. Exp. Biol. Med.*, 1958, (1), 181–185.—A method for the separation of ebrospinal fluid proteins is presented and its ue discussed. A technique for staining lyo- teins in cerebrospinal fluid and serum is cribed. B. P. Block

696. **Technique for separation of protein by ans of agar-gel electrophoresis.** B. Zak and K. M. (Dept. Path., Wayne State Univ. Coll. of Med., roit, Mich., U.S.A.). *Amer. J. Clin. Path.*, 8, **29** (1), 69–79.—A simple method is described the preparation of electropherograms on dil. r in barbitone buffer (pH 8·6) supported on glass tes. After electrophoresis, the plates are dried l stained by the conventional reagents. The ed stained plate is then treated with immersion and covered with another glass plate to obtain eased clarity of the background. The extinc- ns of the stained zones are measured at 610 m$\mu$ a densitometer. This procedure precludes efacts resulting from scattering of light by fibres t are normally encountered in paper electro- resis. The technique has been applied to the aration, identification and quant. determination proteins in serum and cerebrospinal fluid and of ormal haemoglobins. P. Nicholls

697. **Determination of free protein mobilities by er electrophoresis with evaporation. I. Evaluation of the buffer flow due to evaporation and tro-osmosis.** K. Schilling and H. Waldmann- er (Biol. Inst., Carlsberg Found., Copenhagen, mark). *Acta Chem. Scand.*, 1959, **13** (1), 1–12 English).—Paper strips resting on nylon threads ween glass plates 6 mm apart were used, and the ent passed was kept constant. A linear relation found between the migration distance of a dextran spot and the distance from the starting point to the strip centre, provided that experiments were confined to the region of uniform buffer concn. in the centre portion of the strip. Equations are given for calculating the evaporation and electro-osmosis parameters. Being constant for a given current, these need not be evaluated if dextran and protein spots are run under identical conditions, as the difference in migration distance equals $mV_t t$, where $m$ = protein mobility on the paper, $V_t$ = voltage at time $t$ when migration is stopped. The $R_F$ of dextran in the buffer used was $\simeq 1$, and its electrophoretic mobility negligible.

**II. Evaluation of temperature and concentration increases, influence of the carrier medium, and measurement of serum-protein mobilities.** H. Waldmann-Meyer and K. Schilling. *Ibid.*, 1959, **13** (1), 13–28.—Protein mobilities in free soln. may be calculated from electrophoresis data by correcting for (*i*) protein adsorption, (*ii*) path-length increase due to paper structure, (*iii*) salt concn. in the migration zone and (*iv*) temp. increase on the strip. (*i*) is evaluated by running a protein and a dextran spot at each end of the paper, each pair at a different distance from the centre. The adsorption factor is $Sp_1 - Sp_2/Sd_1 - Sd_2$, where $Sp$ and $Sd$ are the migration distances for protein and dextran, respectively. It varies with buffer concn.; (*ii*) is obtained by comparing the conductivities of moist paper and an equivalent buffer column, and is constant for a given brand of paper; (*iii*) is a function of the input of watts, and must be found for the apparatus used; (*iv*) is calculated from the "dextran shrinkage" (the distance between starting positions divided by the distance between final positions). Free mobilities of serum albumin and $\gamma$-globulin calculated from the final equation agreed excellently with moving boundary data. D. G. Moss

3698. **New method for starch-gel electrophoresis of human haemoglobins, with special reference to the determination of haemoglobin $A_2$.** C. A. J. Goldberg (William Pepper Lab. of Clin. Med., Univ. of Pennsylvania, Philadelphia, U.S.A.). *Clin. Chem.*, 1958, **4** (6), 484–495.—The method differs from that previously described (Goldberg, *Scand. Clin. Lab. Invest.*, 1957, **10** (suppl. 31), 273) in the use of a discontinuous buffer system. The starch bed is made with buffer soln. (pH 9·0) composed of tri(hydroxymethyl)methylamine (6·05 g), disodium EDTA dihydrate (0·780 g) and $H_3BO_3$ (0·460 g) dissolved in water and the vol. made up to 2 litres. Barbitone buffer soln. (0·06 *M*) (pH 8·6) is used in the electrode vessels.

H. F. W. Kirkpatrick

3699. **Detection of haemoglobin, haemoglobin - haptoglobin complexes and other substances with peroxidase activity after zone electrophoresis.** J. A. Owen, H. J. Silberman and C. Got (Dept. of Biochem., Univ. of Melbourne, Carlton, Victoria, Australia). *Nature*, 1958, **182**, 1373.—Comparison of various reagents showed *o*-dianisidine to be the most satisfactory. This substance (100 mg) is dissolved in ethanol (70 ml); 1·5 *M* acetate buffer soln., pH 4·7 (10 ml) and $H_2O$ (18 ml) are added. Immediately before use 100-vol. $H_2O_2$ (2 ml) is added to this soln. After electrophoresis, paper or starch-gel strips are placed in the reagent for 15 min. and are then washed in 3 changes of water and dried. Zones possessing peroxidase activity are stained brown - pink. H. F. W. Kirkpatrick

3700. **Human haptoglobins: estimation and purification.** G. E. Connell and O. Smithies (Dept. of Biochem., Univ. of Toronto, Canada). *Biochem. J.*, 1959, **72** (1), 115–121.—A rapid and accurate method for the determination of haptoglobulin in serum or in purified preparations depends on the peroxidase activity of haemoglobin - haptoglobin complexes, $H_2O_2$ and guaiacol being used as the oxidising substrate and H donor, respectively. Reaction conditions are chosen so that the peroxidase activity of free haemoglobin is essentially zero. The formation of tetraguaiacol during the reaction is followed spectrophotometrically. The method is calibrated against a haemoglobin standard so that the haptoglobin content of a soln. can be expressed in terms of its haemoglobin binding capacity.
J. N. Ashley

3701. **Method for accurate determination of plasma albumin.** E. L. Kanabrocki, J. Greco, R. L. Veatch and L. Wilkoff (Veterans Admin. Hosp., Hines, Ill., U.S.A.). *J. Lab. Clin. Med.*, 1958, **52** (4), 661–666.—Errors arising from inconsistency in salting-out are minimised by the method described. Results for plasma albumin agree well with those obtained by electrophoresis. *Procedure*—To 0·25 ml of plasma in a test-tube (16 mm × 125 mm) add 7·75 ml of 26·8% $Na_2SO_4$ soln. at 37° and overlay with 3 ml of diethyl ether. Stopper the tube, invert 11 times in 30 sec. and then centrifuge at 900 *g* for 10 min. Tilt the tube to loosen the globulin layer and remove 2·0 ml of the underlying liquid for determination of N by the micro-Kjeldahl method.
W. H. C. Shaw

3702. **Improved periodic acid - fuchsine - sulphite staining method for evaluation of glycoproteins.** W. F. McGuckin and B. F. McKenzie (Sect. of Biochem., Mayo Clinic, Rochester, Minn., U.S.A.). *Clin. Chem.*, 1958, **4** (6), 476–483.—The method of Köiw and Grönwall (*Scand. J. Clin. Lab. Invest.*, 1952, **4**, 244) requires modification for application to the heavier type of filter-paper (Whatman 3MM). Preliminary washing of the dried strip with 95% ethanol is essential to remove buffer salts and ensure a suitable pH for oxidation, and the oxidation must be controlled at 20° ± 0·5° for 12 min. to ensure low background colour. Reduction with a metabisulphite - thiosulphate reagent is superior to the original method. The concn. of HCl in the dye bath and wash soln. is critical in affecting the quality of the staining. Preparation of the modified reagents and of the sample for analysis is described.
H. F. W. Kirkpatrick

3703. **Method for assaying for glycoprotein in calcium fractionation.** B. Ravinowitch and R. Bartosiewicz (Argonne Cancer Res. Hosp., Univ., Chicago, Ill., U.S.A.). *Proc. Soc. Exp. Biol. Med.*, 1958, **99** (1), 42–43.—A method for the quant. or qual. determination of carbohydrate in samples involves the deposition of micro quantities of the samples on paper strips, staining with Köiw's stain and analysis of the results with the Spinco Analytol apparatus. The procedure has been described by Köiw and Grönwall (*J. Clin. Lab. Invest.*, 1952, **4**, 244).
B. P. Block

3704. **Improvement in the protein-bound iodine method.** H. W. Marlow (Vet. Admin. Hosp., Downey, Ill., U.S.A.). *Clin. Chem.*, 1958, **4** (6), 510–512.—The addition of a specified amount of $KClO_3$ to the mixture in the incineration procedure eliminates unburned residue and shortens the time of heating.
H. F. W. Kirkpatrick

3705. **Modification of the alkaline combusti method for the determination of protein-bou iodine in serum.** P. Vilkki (Surgical Clinic a Dept. of Pharmacol., Univ. of Turku, Finlan *Scand. J. Clin. Lab. Invest.*, 1958, **10** (3), 272–277. In the method of Barker *et al.* (*J. Clin. Inves* 1951, **30**, 55), pptn. of proteins is replaced dialysis in Cellophane bags against tap water. T water used must not contain >10 μg of iodine p litre, and dialysis must continue for ⩽12 hr. T dialysis bags and contents are ashed with an alkal catalyst reagent (70·1 g of KOH and 25·0 g $ZnSO_4$, each dissolved in 250 ml of $H_2O$ and mix immediately before use), in nickel crucibles at 60 followed by extraction of the ash with stro alkali. The recovery of added iodide, which checked with each series of analyses, shows that t dialysis procedure extracts all inorganic iodid The modified procedure gave a mean value f protein-bound iodine in 20 sera which was 0·26 per 100 ml higher than that obtained by pptn but this is not significant. The method is suitab for the determination of iodine in other tissues a in foodstuffs.
D. W. Moss

3706. **Spectrophotometry in the far-ultra-viol region. II. Absorption spectra of steroids a triterpenoids.** D. W. Turner (Imperial Coll., Lo don). *J. Chem. Soc.*, 1959, 30–33.—The spect of some 36 steroids and triterpenoids and oth simpler compounds are corrected for the hig intensity absorption at 176 mμ (related to t number of quaternary C centres) by subtraction the spectrum of the dihydro compound. T $\lambda_{max.}$ of the corrected curves resemble those simpler olefins and are correlated with the degree double-bond substitution (4 substituents, 200 196; 3, 193 to 188; 2, 188 to 182 mμ). As exce tions, geminally di-substituted olefins absorb abnormally long wavelengths (attributable to dipole-moment vector effect), and a bathochrom shift is observed in certain members of the t substituted group, particularly in $\Delta^7$-compound The attribution of the second type of exception steric strain is discussed.
E. J. H. Birch

3707. **Mass spectra of steroids.** S. S. Friedlan G. H. Lane, jun., R. T. Longman, K. E. Train a M. J. O'Neal, jun. (Dept. of Physics, Univ. Connecticut, Storrs, U.S.A.). *Anal. Chem.*, 195 **31** (2), 169–174.—Pyrolysis of the sample at 35 for 30 min. followed by mass spectrometry giv results sufficiently reproducible for the identificati of a single steroid and for the quant. analysis simple mixtures. By the use of a heated (200 gas-inlet system in a mass spectrometer, characte istic cracking patterns are obtained which gi much information about the molecular structu as well as the molecular weight of the sampl About 1 mg of sample is adequate.
A. R. Rogers

3708. **Isolation, characterisation and measur ment of steroid glucuronides in human plasm** G. L. Cohn and P. K. Bondy (Dept. of Internal Me Yale Univ. Sch. of Med., New Haven, Con U.S.A.). *J. Biol. Chem.*, 1959, **234** (1), 31–34.— method is described for the determination of t glucuronides of tetrahydrocortisone and tetr hydrocortisol in plasma. The conjugated steroi are separated from the non-conjugated steroids paper electrophoresis and paper chromatograph Each glucuronide is then determined by t carbazole reaction. An isotope dilution method

described; it is used with [4-$^{14}$C]tetrahydro-isone glucuronide to correct the results to 100% very. J. N. Ashley

709. **Isolation of oxosteroids under neutral ditions.** W. Taylor (Physiol. Dept., Med. Sch., g's College, Newcastle upon Tyne). *Nature*, 8, **182**, 1735.—The method of Teitelbaum (*J. Chem.*, 1958, **23**, 646) for the isolation of labile ones has been applied to the ketosteroids pro-erone (**I**) and pregnanediolone (**II**). Dissolve steroid (10 mg) in ethanol (1 ml) and add Girard gent T (20 mg) and Amberlite IRC-50 cation-hange resin (5 mg). Heat under reflux for 1 hr. llow to stand at room temp. for 24 hr. Add (10 ml) and extract non-ketonic material with ent (diethyl ether for **I** or ethyl acetate for **II**). 40% formaldehyde soln. (2 ml), allow to stand rnight and extract the ketosteroid with solvent. recovery is >90%, with <1% appearing in the -ketonic fraction. A. R. Rogers

710. **Spectrophotometric determination of $\triangle^{4}$-3-steroids with salicylhydrazide. Application urinary aldosterone.** P. S. Chen, jun. (Sect. of . Endocrinol., Nat. Heart Inst., Nat. Inst. of alth, Bethesda, Md., U.S.A.). *Anal. Chem.*, 9, **31** (2), 292–296.—Salicylhydrazide reacts h cortisone, cortisol, aldosterone, corticosterone, osterone and progesterone to form characteristic drazones which absorb strongly at 295 m$\mu$. eir analytical use is exemplified by the determina- of aldosterone in urine. *Procedure*—Extract urine at pH 1 with dichloromethane for 20 hr. rify the extract by paper chromatography, first h the C system of Bush (*Biochem. J.*, 1952, **50**, ), and then with the $E_2B$ system of Eberlein Bongiovanni (*cf. Anal. Abstr.*, 1956, **3**, 3160). te the aldosterone zone with ethanol, evaporate dryness and allow to react with salicylhydrazide thanolic acetic acid at 60° for 30 min. Remove ess of reagents and other impurities by paper-omatographic development with benzene satd. h $H_2O$; aldosterone salicylhydrazone remains the origin. Extract with 50% ethanol and asure the extinction at 295 m$\mu$; correct for the er-paper blank by the method of Allen (*J. n. Endocrinol.*, 1950, **10**, 71). A loss of about % of the steroid occurs at each chromatographic aration step, and a correction should be applied. e results of 6 replicate determinations of aldo-rone in a 6-hr. urine sample ranged from 15·8 20·1 $\mu$g. A. R. Rogers

711. **Production of fungal amylase. I. Fuwa's thod of determination of $\beta$-amylase.** Nobuhiko mada (Inst. for Fermentation, Juso-Nishino-cho, gashi-yodogawa-ku, Osaka). *J. Agric. Chem. Japan*, 1958, **32** (8), 581–583.—Fuwa's method the determination of $\beta$-amylase (**I**) with amylose 0·5 *M* acetate buffer (*J. Biochem. Japan*, 1954, 583) was kinetically examined with reference to application to the determination of low concn. of By decreasing the final vol., the limit of deter-ation was decreased to one tenth. The hydroly- apparently proceeds as a first-order reaction; amount of the reagents must not be decreased. sample soln. (10 ml) is mixed with 0·5 *M* acetate fer (pH 5·4) and 0·2% amylose soln., and kept at for 30 min.; the resulting sugar is determined by son's molybdoarsenate method (vol. 10 ml).
K. Saito

3712. **Carbonic anhydrase. A spectrophotometric assay.** P. K. Datta and T. H. Shepard (Washington Univ., Seattle, U.S.A.). *Arch. Biochem. Biophys.*, 1959, **79**, 136–145.—In the method described, 1·0 ml of aq. phenol red soln. (pH 6·0), containing 12·5 $\mu$g of indicator, and 1·5 ml of water are placed in the reference cell of a recording spectrophotometer set at 560 m$\mu$. In the sample cell are placed 1·0 ml of the same phenol red soln. and 1·5 ml of test soln. or water. Both soln. are equilibrated for 2 min. in the cell compartment maintained at 4° to 5° with cooled 95% ethanol, while $CO_2$ (12 ml per min.) is passed through the cells. After recording the base line, 1·0 ml of 0·0286 *M* tri(hydroxymethyl)-methylamine buffer (pH 9) is injected into the sample cell, and the time taken for the extinction difference to fall to 0·20 is measured. The difference in time required for this to occur for water and for the test soln. is a measure of enzyme activity.
W. H. C. Shaw

3713. **Rapid colorimetric method for the quantitative determination of copper oxidase activity (ceruloplasmin).** O. B. Houchin (Dept. of Neurol., Univ. of Arkansas Sch. of Med., Little Rock, U.S.A.). *Clin. Chem.*, 1958, **4** (6), 519–523.—*Procedure*—To 1·0 ml of freshly prepared 0·1% *p*-phenylenediamine in acetate buffer (pH 5·2) at 37°, serum (0·1 ml) is added. After incubation for 15 min. at 37°, 0·02% sodium azide soln. (5·0 ml) is added to stop the reaction, and the extinction is read against a blank (water or reagent) at 525 m$\mu$. Correlation of the extinction with ceruloplasmin concn. determined by the method of Scheinberg *et al.* (*Science*, 1957, **126**, 925) is employed for calibration and shows a straight-line relationship.
H. F. W. Kirkpatrick

3714. **Colorimetric micro-method for the determination of cholinesterase.** D. E. McOsker and L. S. Daniel (Cornell Univ., Ithaca, N.Y., U.S.A.). *Arch. Biochem. Biophys.*, 1959, **79**, 1–7.—A rapid sensitive method is described for the determination of cholinesterase activity, with acetylthiocholine as substrate. The method is applied to the assay of animal brain, blood and plasma. *Procedure*—Place, in a 15-ml centrifuge tube, 0·20 ml of 0·015 *M* acetylthiocholine iodide, 0·50 ml of 0·125 *M* tri-(hydroxymethyl)methylamine buffer (pH 7·4), 0·20 ml of 3·5 *M* NaCl and water to 1·30 ml. Warm to 37°, add 0·10 ml of tissue homogenate and incubate for 10 min. Add 0·10 ml of 25% w/v trichloro-acetic acid (or of 50% w/v soln., if necessary to produce a clear supernatant liquid) and centrifuge. Place in a spectrophotometer cell 2·0 ml of satd. aq. NaCl soln., 0·4 ml of $Na_2CO_3$ - NaCN soln. (21·2 g of $Na_2CO_3$ and 0·44 g of NaCN in water to 100 ml) and 0·4 ml of sodium nitroprusside soln. (27 mg per ml). Mix, add 0·2 ml of the supernatant liquid and after exactly 30 sec. measure the extinction at 520 m$\mu$. W. H. C. Shaw

3715. **Investigations on the enzymes of human blood. I. Photometric micro-determination of acetylcholinesterase in serum and erythrocytes.** W. Pilz (Ärzlich. Abt., Farbenfabrik: A.-G., Bayer, Leverkusen, Germany). *Klin. Wochschr.*, 1958, **36** (21), 1017–1021.—The rapid method described requires 0·02 ml of blood, and is based on measurement at 490 m$\mu$ of the red colour formed when $Fe^{3+}$ react with acetohydroxamic acid produced by the action of unchanged acetylcholine on hydroxyl-

amine in alkaline soln. The various factors affecting the determination were investigated, including the specificity of the enzyme for different substrates. D. B. PALMER

3716. **Glutamic - aspartic transaminase. I. Assay, purification and general properties.** W. T. Jenkins, D. A. Yphantis and I. W. Sizer (Div. of Biochem., Dept. of Biol., M.I.T., Cambridge, Mass., U.S.A.). *J. Biol. Chem.*, 1959, **234** (1), 51–57.—A spectrophotometric method is described for the assay of the transaminase. It is based on the determination, at 280 mμ, of the enol form of oxaloacetate which is in equilibrium with the oxo form produced in the reaction between aspartate and α-oxoglutarate in the presence of the enzyme. J. N. ASHLEY

3717. **Stable test-papers for seminal acid phosphatase.** S. S. Kind (Home Office Forensic Sci. Lab., Rutland Drive, Harrogate, Yorks., England). *Nature*, 1958, **182**, 1372–1373.—Dissolve 1-naphthyl phosphoric acid (200 mg) and diazo-*o*-dianisidine (Brentamine Fast Blue B Salt) (C.I. Azoic Diazo Component 48) (400 mg) in 0·2 *M* citric acid - Na citrate buffer soln., pH 4·9 (100 ml); soak a filter-paper in this soln. and allow to dry at room temp. in subdued light. Store in a light-proof bottle. Apply a wet filter-paper to the stain and place a moistened test-paper on this; a positive reaction is shown by an intense purple colour formed on the intermediate paper. The test-paper remains usable for a year. H. F. W. KIRKPATRICK

3718. **Studies on sulphatases. XXIV. Use of barium chloranilate in the determination of enzymically liberated sulphate.** A. G. Lloyd (Dept. of Biochem., Univ. of Wales, Newport Rd., Cardiff). *Biochem. J.*, 1959, **72** (1), 133–136.—A modification of the Ba chloranilate method (*cf.* Bertolacini and Barney, *Anal. Abstr.*, 1957, **4**, 2580) is described for the determination of small amounts (5 to 80 μg per 0·2 ml) of sulphate. After the pptn. of $BaSO_4$, the amount of chloranilate ion released into the soln. is determined at 350 mμ. There is a linear relation between the concn. of sulphate and the spectrophotometric reading. The presence of other anions does not affect the result, but $NH_4^+$, $Ca^{2+}$, $Co^{2+}$, $Mn^{2+}$, $Fe^{2+}$, $Pb^{2+}$ and $Cu^{2+}$ interfere. The method, which effects a considerable saving in time, compares favourably with the benzidine method. Within certain limits the assay is unaffected by the presence of the assay substrates for carbohydrate sulphatases. J. N. ASHLEY

3719. **The electrophoresis and titration of fumarase.** [**Determination of fumarase.**] N. Shavit, R. G. Wolfe and R. A. Alberty (Dept. of Chem., Univ., Wisconsin, Madison, U.S.A.). *J. Biol. Chem.*, 1958, **233** (6), 1382–1386.—The concn. of active enzyme in a soln. is determined by adding L-malate and determining the steady-state rate of dehydration to fumaric acid from the rate of change of absorbance in the u.v. region. The enzyme soln. is diluted with 0·05 *M* phosphate buffer (pH 7·3). To the dil. soln. (3 ml) add 0·35 *M* K L-malate (0·5 ml) which also contains 0·05 *M* phosphate buffer. Measure the change in absorbance per 10 sec. at 250 mμ, with a 1-cm cell. The change in absorbance divided by 31·5 gives the amount of fumarase in mg in 3 ml of the dil. soln. J. N. ASHLEY

3720. **The presence of pyruvate as a source error in ammonia determinations by means Nessler's reagent.** G. Steensholt and L. Rotn (Dept. of Biochem., Oslo Univ., Norway). *A Chem. Scand.*, 1959, **13** (1), 189–190 (in English). The colours of Nessler reagent with added NH were reduced in the presence of pyruvate (1 μmoles per 9 ml of final soln.) by about 50% Vanselow's, and 24% for Kolthoff's, Nessler reage both used with Archibald's persulphate - glucona stabiliser. For the determination of pyruva activated glucaminase II, a calibration curve p pared by adding pyruvate to the $NH_4^+$ standar should be used. To allow for loss of pyruva during incubation, 80% of the initial amount pyruvate should be added to the blank, after addi $H_2SO_4$ on termination of the incubation (Beato *Proc. Soc. Exp. Biol. Med.*, 1954, **87**, 238). D. G. Moss

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*See also Abstracts*—**3457**, Determination of $NH_3$ biological fluids. **3495**, Chlorine in distilled wat as a source of error. **3503**, Determination of iodi in serum. **3584**, Determination of cysteine. **360** Catecholamines in urine. **3648**, Determination Ca in serum. **3745**, Determination of thiohyda toins in urine. **3763**, Determination of lysine milk. **3769**, Phenolic constituents in *Prun domestica*. **3780**, Unsaturated fatty acids plasma. **3785**, Microbiological assay of ami acids. **3813**, Sedimentation analysis. **3818**, Fra tion collector for amino acids. **3820**, Chromat graphy of amino acids. **3823**, Chromatography quaternary ammonium compounds. **3852**, Sodiu in biological systems. **3854**, Source of error radioactive counting.

## Pharmaceutical analysis

3721. **Modern analytical chemistry in the servi of pharmacy and medicine.** G. E. Foster (Wellcon Chem. Works, Dartford, Kent, England). *Pharm. Pharmacol.*, 1958, **10**, Supplement, 9T–23 —A review with 59 references. A. R. ROGERS

3722. **Colorimetric determination of morphine galenical preparations.** C. A. Johnson and C. Lloyd (Standards Dept., Boots Pure Drug Co. Ltd Nottingham, England). *J. Pharm. Pharmaco* 1958, **10**, Supplement, 60T–71T.—Improved extra tion procedures are suggested for the separation morphine from extraneous material in camphorate tincture of opium, opiate linctus of squill, compour camphorated linctus of opium, ammoniated tinctu of opium, opiate pastilles of squill and tincture chloroform and morphine (*cf.* Garratt *et al.*, *Ana Abstr.*, 1958, **5**, 2754). The application of th colorimetric method of Pride and Stern (*cf. Ana Abstr.*, 1954, **1**, 3093) to the morphine residues obtained is described. A. R. ROGERS

3723. **Comparative study of the hydrolytic a non-hydrolytic methods for the assay of solanaceou drugs.** R. E. A. Drey (Wellcome Chem. Work Dartford, Kent, England). *J. Pharm. Pharmac* 1958, **10**, Supplement, 241T–246T.—The resul obtained by the hydrolytic and non-hydrolyt methods for the determination of the total alkalo content are in good agreement for belladonn stramonium and hyoscyamus. The agreement fair for *Duboisia leichhardtii* and *Datura sanguine* whilst for *Duboisia myoporoides* the non-hydrolyt

hod gives spuriously high results. The hydro- method is recommended for the assay of ysia samples and for Indian belladonna. ne, tropine, belladonnine, hyoscine, valeroidine, idine and apoatropine can be separated from other and from hyoscyamine and norhyo- mine by descending chromatography, on What- No. 1 paper treated with 0·2 *M* KCl, with a -saturated mixture of *n*-butanol - *n*-butyl ate - glacial acetic acid (3:17:8) as solvent.

A. R. Rogers

724. **Interference of autoxidised ether in analysis lkaloids and other organic bases. III. Deter- ation of alkaloids of belladonna extract.** B. dahl and E. H. Vihovde (Pharm. Chem. Lab., ., Oslo, Norway). *Medd. Norsk Farm. Selsk.*, 9, **21** (1), 1–8.—When treated with diethyl ether aining 0·1% of peroxides (as $H_2O_2$) under the litions obtaining in the Norwegian official hod for the determination of alkaloids in the act, hyoscyamine is shown by paper-chromato- hic analysis to be completely oxidised to hyoscyamine. The effect of ether containing 5% of peroxides is negligible. Similar results obtained for atropine. As the genoalkaloids not titratable with HCl to methyl red, the tion results obtained after the use of autoxidised r will be low. These results are analogous to e found for the nux vomica alkaloids (*cf. l. Abstr.*, 1959, **6**, 2745). P. S. Arup

725. **Quantitative determination of the sum of loids belonging to various groups in ergot.** Speichert (Inst. of Medicinal Plants, Poznan). *Polon. Pharm.*, 1959, **16** (1), 51–56.—A new hod for the quant. determination of the alkaloids nging to three groups (ergometrine, ergotamine ergotoxine) has been developed. An aliquot he pulverised and de-fatted ergot is extracted diethyl ether and the ether extract is placed a non-impregnated Whatman No. 3 paper. mobile phase comprises benzene - toluene - t petroleum - methanol (12:5:5:2). Develop- t of the chromatogram takes ≃3 hr. Quant. lts are obtained by eluting the cut-out spots of alkaloid groups with a 0·5% soln. of tartaric in methanol and developing the colour with ort's reagent; semi-quant. results are obtained comparing a chromatogram of pure alkaloid dards with that of the tested extract in u.v. t. W. B. Miaskowski

726. **Micro-identification of rauwolfia alkaloids paper electrophoresis and multi-buffered paper matography.** Hidehiko Kaneko (Res. Lab., nihon Pharm. Co., Kami-ebie, Fukushima-ku, ka). *J. Pharm. Soc. Japan*, 1958, **78** (5), 512–—Nine alkaloids in Indian snakewood (*Rau- a serpentina* Benth.) were separated by paper trophoresis (500 V, 2 to 4 hr.) with 0·1 *N* citric or *N* acetic acid as electrolyte. Each spot was cted by fluorescence or with Dragendorff ent. The rate of migration increased in the r rescinnamine, reserpine, reserpinine, serpen- sarpagine, ajmalicine, yohimbine, ajmaline serpentinine. By multi-buffered paper chro- ography with $CHCl_3$ - benzene (1:2), *i.e.*, the use of a paper impregnated at regular rvals with citrate buffers of pH 6·4, 5·8, 5·5, 4·9, 4·6, 4·3, 4·0, 3·0 and 2·1, the spots of these loids were found at pH 4·3, 4·6, 3·0, 7·0, 7·0, 5·5, 6·1 and 6·4, respectively (at pH 7·0 the s remain at the origin). K. Saito

3727. **Decomposition products of reserpine and their influence on the determination of reserpine.** K. G. Krebs and N. Futscher (Univ.-Apotheke, Tübingen, Germany). *Dtsch. ApothZtg*, 1958, **98** (52), 1341–1344.—Deteriorated preparations of reserpine (**I**) give results by the column-chromatographic method of Bartelt and Hamlow (*cf. Anal. Abstr.*, 1956, **3**, 1478) and the fluorimetric method of McMullen *et al.* (*Ibid.*, 1956, **3**, 509) which accord with the stated content of **I**, whilst the colorimetric vanillin - HCl method of Banes (*Ibid.*, 1956, **3**, 510) gives much lower results. It is found that the primary product of the decomposition of **I** (possibly 3:4-dehydroreserpine), which appears in chromatograms as a green spot under u.v. light, gives no coloration with vanillin and HCl. A spectrophotometric method is described for the determination of **I** which depends on the quant. conversion of **I** into the primary decomposition product by treatment under standard conditions with $NaNO_2$ and acetic acid; the product is distinguished by a specific absorption maximum at 388 mμ. Comparisons are made with similarly treated soln. of pure **I**. The content of the decomposition product originally present in deteriorated samples is determined by spectrophotometric measurement of untreated soln. of the samples, and deducted from the total. The reproducibility of the method is satisfactory. Results are accurate to within ±1·2% for tablets, and ±0·7% for soln. Drugs commonly used in combination with **I**, or substances used in preparing tablets, do not interfere. P. S. Arup

3728. **Detection reactions for 1-(dihydroxypropyl)- theobromine and 7-(dihydroxypropyl)theophylline and a critical comparison with those for caffeine, theobromine and theophylline.** R. Ott and (in part) H. Wittmann-Zinke (Inst. für Organ. und Pharm. Chem., Univ., Graz). *Sci. Pharm.*, 1958, **26** (4), 217–224.—A review is presented, with 26 references, of pptn. and colour tests and paper-chromatographic methods of detection of caffeine, theobromine and theophylline. The behaviour of 1-(dihydroxypropyl)theobromine and 7-(dihydroxypropyl)theophylline in these tests is described.

A. R. Rogers

3729. **Determination of alkaloids in aluminium oxide columns. II. Caffeine in caffeine citrate, caffeine sodium salicylate, caffeine sodium benzoate, caffeine benzoate, "Coffea" tincture HAB, filtered coffee and Nescafé powder.** K. Pfandl (Wissenschaftl. Abteil. der Firma Chem.-pharm. Fabrik, Müller/Göppingen). *Dtsch. ApothZtg*, 1959, **99**, 141–143.—Caffeine may be determined in these preparations by passing them, in a water - ethanol medium, through a chromatographic column of basic aluminium oxide. A mixture of $CHCl_3$ and diethyl ether, used as eluent, dissolves the caffeine, which is then weighed after evaporation of the solvent. M. H. Sawistowska

3730. **Digitalis glycosides. II. Influence of method of drug extraction on results of paper-chromatographic analysis of digitalis leaves (*Digitalis lanata* Ehrh. and *D. purpurea* L.).** L. Fuchs, M. Wichtl and H. Jachs (Pharmakog. Inst. Univ., Wien). *Arch. Pharm., Berlin*, 1959, **292** (1), 15–20.—Procedures for hot and cold extraction of digitalis leaves with water and 20% and 70% ethanol are described. Paper-chromatographic analysis shows the highest content of glycosides in the hot 70% ethanol extract. With cold-water extraction, substantial fermentative degradation of primary glycosides takes place. M. H. Sawistowska

3731. **Chemical evaluation of digitalis drugs (*Digitalis purpurea* and *D. lanata*). Preliminary report.** W. Hauser and I. Mathauser (Pharmakog. Inst. Univ., Graz). *Sci. Pharm.*, 1958, **26** (4), 258–262.—The use of Pb acetate in the purification of aq. extracts of digitalis before assay may lead to losses of glycosides of up to 14%; with basic Pb acetate, losses may be up to 30%. In the method described, interference caused by flavones is eliminated by use of CaO. *Procedure*—Dilute the filtered hot-water extract (50 ml ≡ 0·5 g of drug) with water (30 ml) and boil gently for 15 min. with dil. HCl (12·5%) (5 ml). Cool, neutralise with dil. aq. $NH_3$ (10%) and extract with diethyl ether (4 × 20 ml). Treat the combined extracts with powdered CaO (2 g) and with anhyd. $Na_2SO_4$ (3 g) and filter. Wash the residue with ether (2 × 15 ml). Evaporate the filtrate and washings to dryness under reduced pressure, dissolve the residue in ethanol (10 ml) and assay by the 3:5-dinitrobenzoic acid method. A. R. Rogers

3732. **Separation and determination of the primary and secondary glycosides of *Digitalis purpurea* leaf.** J. Lemli (Lab. de Pharmacog., Inst. de Pharm., Louvain, Belgium). *Pharm. Acta Helv.*, 1959, **34** (1), 19–28 (in French).—Prepare a 1:10 tincture with 70% ethanol and transfer to a chromatographic column of $Al_2O_3$ (Brockmann grade III). Elute chlorophyll and other coloured matter with diethyl ether and discard. Elute digitoxin, odoroside H, gitoxin, gitaloxin, strospeside, verodoxin and derivatives of diginin with $CHCl_3$ - methanol (9:1). Pass more ether through the column, and then elute purpurea glycosides A and B, glucogitaloxin, digitalinum verum and gitorin with 35% aq. ethanol. The glycosides are determined colorimetrically in alkaline ethanolic soln. at 540 mμ by the 3:5-dinitrobenzoic acid reaction after hydrolysis with 0·4 *N* HCl to the aglycones. Some species of digitalis contain colouring matter which is insol. in ether but sol. in $CHCl_3$ - methanol (9:1) and causes interference; this is corrected by using as a blank an alkaline soln. of the eluate which has not been treated with 3:5-dinitrobenzoic acid.

A. R. Rogers

3733. **Reaction between dinitro derivatives and active methylene compounds. I. Colorimetric determination of cardiotonic glycosides with 3:5-dinitrobenzenesulphonic acid.** Masami Akatsuka (Pharm. Fac., Kumamoto Univ., Kihonji). *J. Pharm. Soc. Japan*, 1958, **78** (1), 62–64.—Potassium 3:5-dinitrobenzenesulphonate (**I**) gives a red colour (max. absorption at 530 mμ) with active methylene compounds such as digitoxin (**II**), strophanthin (**III**) and ouabain (**IV**) in alkaline soln. The extinction is proportional to the concn. of **II**, **III** and **IV** for <10 mg per 100 ml. With increase in concn. of alkali, the colour develops and fades faster. The sample is extracted with methanol and diluted, and a 4-ml aliquot is mixed with **I** soln. (5%) (0·5 ml) and KOH soln. (5%) (0·5 ml); the extinction is measured at 530 mμ after 10 min.

K. Saito

3734. **Application of a spectrophotometric method to the determination of potassium penicillin, procaine penicillin and benzathine penicillin in pharmaceutical preparations.** A. Holbrook (I.C.I., Ltd., Pharmaceuticals Div., Blackley, Manchester). *J. Pharm. Pharmacol.*, 1958, **10** (12), 762–769.—Penicillin is determined spectrophotometrically after degradation to penicillinic acid by heating with acetate buffer (pH 4·6) in the presence of a trace of $Cu^{2+}$. The method has a standard error of 3% It is applicable to a variety of ointments, lozeng injections and other preparations of penicillin af preparation of an appropriate extract. The resu are in good agreement with those obtained mic biologically. A. R. Rogers

3735. **Colorimetric estimation of phenoxymeth penicillin (penicillin V) and phenoxyacetic acid samples from penicillin fermentations.** J. Birn (Commonwealth Serum Lab., Melbourne, Australi *Anal. Chem.*, 1959, **31** (2), 271–273.—The meth depends on the yellow colour given in ammonia soln. by the derivatives formed by the nitration phenoxymethylpenicilloic acid (**I**) [the product alkaline hydrolysis of penicillin V (**II**)] and phenoxyacetic acid (**III**); **III**, but not **I**, is extract by benzene from a satd. aq. soln. of $(NH_4)_2SO_4$ pH 2; both **I** and **III** are extracted by *iso*but methyl ketone from a similar soln. As little 12 μg of **II** and 5 μg of **III** can be determined.

A. R. Rogers

3736. **Chromatograpic assay method for dete mining insulin in whale pancreas extract.** Yuic Sasano and Katsumi Higashi (Res. Lab., Tai Fisheries Co., Tsukishima, Chuo-ku, Tokyo). *Pharm. Soc. Japan*, 1958, **78** (4), 424–427.—F the paper-chromatographic separation of insu (**I**) ($R_F$ 0·21 to 0·26) with a mixture of acetic ac butanol and water (1:6:7, by vol.) (*cf. An Abstr.*, 1957, **4**, 3426), the total protein must <3 mg and the total electrolyte <5 mg (as $NH_4C$ The electrolytes are removed by dialysis and **I** concentrated by evaporation at 30° to 34°. The sp is stained with 0·02% bromocresol green and t combined indicator is extracted from the cut-o spot with borate - NaOH buffer, and the extincti is measured at 620 mμ. K. Saito

3737. **Quantitative determination of nicoti acid in some pharmaceutical preparations with t aid of cation exchanger Wofatit KPS-200.** Howorka (Staatl. Inst. für Arzneimittelprüf., Jen *Pharm. Zentralh.*, 1958, **97** (11), 521–524.— determine sodium nicotinate, apply an aq. soln. the sample (50 to 250 mg) to a column of Wofa KPS-200 in the pyridine form, elute with H (250 ml), and titrate the eluate with 0·1 *N* KO Perform a blank titration to compensate for C in the water. Compensate for the presence mineral salts by titration of the eluate resulti from the passage of a duplicate sample through column of the $H^+$ form of the resin. Esters a amides of nicotinic acid and preparations may assayed by application of the method to t products of saponification. A. R. Rogers

3738. **Assay of nicotinamide in tablets and inje tions by non-aqueous titration.** H. H. Kavara (Anal. and Standardisation Dept., Worli Che Works, Bombay, India). *Indian J. Pharm.*, 19 **20** (12), 360–361.—Nicotinamide in B-compl tablets and injections is separated from interferi substances by its solubility in acetone, and titrated with $HClO_4$ in glacial acetic acid. *P cedure*—A sample of B-complex tablet containi ≃100 mg of nicotinamide is extracted with aceto (6 × 20 ml) and the filtrate is evaporated to dryne The dry residue is dissolved in 20 ml of glac acetic acid and 12 drops of methyl violet (0·2 w/v in chlorobenzene) are added. On titrati with 0·1 *N* $HClO_4$ in glacial acetic acid the wine-r colour turns green on the approach of the end-poi

ıd the end-point is reached when a yellow colour ersists for 1 min. The acid is standardised with 90 mg of pure nicotinamide, and a permanent blue olour indicates the end-point. Injections are aporated to dryness and the residue treated in ıe same way as the tablets. Riboflavine does not terfere except in large excess (unlikely in practice). xcipients (not containing glucose or sucrose), sintegrating agents and even chocolate coating o not interfere. Preparations in a syrup or malt ase cannot be determined in this way owing to complete extraction of the sticky residue by etone. E. J. H. Birch

3739. **Studies on streptomycetes. Assay of vitamin $B_{12}$ in the presence of dihydrostreptomycin.** Koiti akazawa, Motoo Shibata, Hiroichi Yamamoto, iji Higashide and Toshihiko Kanzaki (Inst. for ermentation, Juso-nishinocho, Higashiyodogawa-u, Osaka). *J. Agric. Chem. Soc. Japan*, 1958, 2 (5), 399–405.—The effect of dihydrostreptomycin ) on the bioassay of $B_{12}$ in a fermenting culture of *treptomyces humidus*, with an *Escherichia coli* utant (No. 313) or *Lactobacillus leichmannii* was xamined. The presence of $<1$ μg or $<0{\cdot}2$μg of per ml of the culture does not cause interference hen *Esch. coli* or *Lb. leichmannii*, respectively, is sed. No interference results from $<2$ μg of other ntibiotics, including oxytetracycline, chloram-henicol, chlortetracycline and penicillin. By uccessive cultivation (12 generations), a strain esistant to 1 mg of **I** per ml was obtained, its esponse towards $B_{12}$ remaining unchanged. The esistant strain is applicable to the determination f $B_{12}$ by the use of a medium containing (per litre) $K_2HPO_4$ (14 g), $KH_2PO_4$ (6 g), $(NH_4)_2SO_4$ (2 g), $MgSO_4.7H_2O$ (0·2 g), citric acid (0·8 g), NaCl (5 g), -asparagine (4 g), DL-tryptophan, L-glutamic acid, -arginine hydrochloride, L-histidine hydrochloride, lycine, proline (0·4 g each) and glucose (4 g).
K. Saito

3740. **Pharmacognostic studies of drugs containing oumarin and its derivatives. III. Chromato-raphic separation and colorimetric determination of mbelliferone and its homologues.** Mitiiti Fujita, sutomu Furuya and Hideji Itokawa (Fac. Pharm., okyo Univ., Hongo). *J. Pharm. Soc. Japan*, 958, **78** (4), 395–398.—The red colour (max. bsorption, 510 mμ) produced by the action of 4-minophenazone (**I**) and $K_3Fe(CN)_6$ on umbelliferone (**II**) in $Na_2CO_3$ soln. obeys Beer's law for $<400$ μg f **II** per ml. The hydrolysis of **II** is complete ithin 20 min. in 0·5% $Na_2CO_3$ soln. The separa-on of **II** from asafoetida, galbanum and ammon-cum (ethanolic extract) is effected by paper ıromatography on paper treated with 0·1 *M* orate, and with butanol satd. with water as eveloping agent. An unidentified sulphur-contain-g substance in asafoetida gives a spot of the same F value, and two-dimensional chromatography is sed with $CHCl_3$ and butanol as developing agents. he spot is cut out, boiled with 0·5% $Na_2CO_3$ soln. 0 ml) for 20 min., cooled for 30 min., mixed with soln. (0·9% aq.) (0·4 ml) and $K_3Fe(CN)_6$ soln. ·4%) (0·2 ml), and the extinction is measured after hr. K. Saito

3741. **Determination of crude fat in crude drugs capillary analysis.** Yoshiaki Okazaki (Public ealth Lab., Marunouchi, Kōchi). *J. Pharm. Soc. apan*, 1958, **78** (6), 684–686.—The use of capillary analysis of the xylene extract of torreyanu, armenica, peanut, datura seed, pharbitis, etc., has been studied. The concn. of fat ($x$) in the xylene is related to the capillary elevation ($y$) by the empirical equation $y = 2^{m-nx}$, where $m$ and $n$ are constants for a given drug. Values of $m$ and $n$ are given for the drugs named. The results agree well with those by the usual Soxhlet extraction method.
K. Saito

3742. **Systematic identification of organic poisons by paper chromatography. I. Detection and separation of hypnotics.** Hisao Tsukamoto and Minoru Yoshimura (Pharm. Inst., Med. Fac., Kyushu Univ., Katakasu, Fukuoka). *J. Pharm. Soc. Japan*, 1958, **78** (1), 23–27.—The $R_F$ values of derivatives of barbituric acid (**I**) (Kaiss and Lang, *Öst. ApothZtg*, 1955, **9**, 558), thiobarbituric acid (**II**) (Heise and Kimbel, *Arzneimittel-Forsch.*, 1955, **5**, 149) and diphenylhydantoin (**III**) (Curry, *Analyst*, 1956, **80**, 901), determined by the use of a mixture of aq. $NH_3$ soln. and organic solvents such as $CHCl_3$, propanol and butanol, decrease with increase in concn. of $NH_3$. It appears that the $R_F$ value decreases with the ease with which enolisation takes place. For the separation of **I** derivatives, a mixture of butanol, $CHCl_3$ and 28% aq. $NH_3$ soln. (3:3:4) is preferred; for the separation of **I** and **II** derivatives, a mixture of *iso*propyl alcohol, acetone and 28% aq. $NH_3$ soln. (5:5:1) is used. By the use of butanol satd. with 10% aq. $NH_3$ soln., the spots of barbiturate, thiobarbiturate, **III** and bromoacylureas (**IV**) can be separated.

**II. Colour reagents for the spot test of hypnotics on filter-paper.** Hisao Tsukamoto and Minoru Yoshimura. *Ibid.*, 1958, **78** (1), 27–29.—Whilst the Cu - pyridine complex (Zwikker, *Pharm. Weekbl.*, 1931, **68**, 975) gives a pink colour with compounds containing the structural units $=N{\cdot}CO{\cdot}N=$, $=N{\cdot}CS{\cdot}N=$ and $=N{\cdot}C:N-$, the use of aq. $AgNO_3$ soln. (0·05%). (Sabatino, *cf. Anal. Abstr.*, 1955, **2**, 1013) permits the separation of **I**, **II** and **IV**. Cobaltammine soln. (*cf.* Posez, *J. Pharm. Chim.*, 1938, **28**, 69) gives a positive reaction with those compounds that have an imino group which is capable of dissociating to give $H^+$. K. Saito

3743. **Applications of nitrometry. XV. Determination of phenazone.** Masaharu Yamagishi, Makoto Yokoo and Saburo Inoue (Res. Lab., Takeda Pharm. Ind., Higashiyodogawa-ku, Osaka). *J. Pharm. Soc. Japan*, 1958, **78** (1), 87–90.—Phenazone is converted within 2 min. to 2-nitrosophenazone (**I**) by the use of $KNO_2$ in dil. $H_2SO_4$, and the excess of $NO_2^-$ is determined, by a nitrometer, with sulphamic acid (**II**). Alternatively, **I** is readily reduced to 2-aminophenazone with zinc dust and the product is determined, by a nitrometer, with **II** and $NaN_3$. K. Saito

3744. **Note on the analysis of diphenylhydantoin sodium by an ion-exchange procedure.** M. C. Vincent and M. I. Blake (N. Dakota Agric. Coll., Sch. of Pharm., Fargo, U.S.A.). *Drug Standards*, 1958, **26** (6), 206–207.—Dissolve the pure diphenylhydantoin sodium (100 mg), or a corresponding quantity of powder from capsules, in dimethylformamide (50 ml) and apply to a column of Amberlite IRC-50 ($H^+$ form) (10 g) which has been soaked in dimethylformamide. Elute with the same solvent and titrate the first 75 ml of eluate with 0·1 *N* Na methoxide in benzene - methanol to a

visual end-point (azo violet indicator) or potentiometrically. The results agree well in accuracy and precision with those by the U.S.P. method for the pure material. It is thought that the U.S.P. method gives low results with capsules. A. R. Rogers

3745. **Fluorimetric assay for minute amounts of some thiohydantoins.** M. E. Auerbach and E. Angell (Anal. Lab., Sterling-Winthrop Res. Inst., Rensselaer, N.Y., U.S.A.). *J. Pharm. Pharmacol.*, 1958, **10** (12), 776–779.—This method has been applied to the determination of 5-*n*-heptyl-2-thiohydantoin and related compounds in urine, plasma and spinal fluid. *Procedure*—Mix the sample, containing $\simeq 1$ μg of thiohydantoin, with phosphate buffer of pH 6·0 (2 ml), dilute to 5 ml with $H_2O$ and shake for 2 min. with $CHCl_3$ (8 ml). Withdraw 5 ml of the $CHCl_3$ layer, evaporate to dryness, cool and dissolve the residue in *iso*propyl alcohol - *iso*butyl alcohol (3:1) (4 ml). Add $H_2O$ (2 ml), aq. $NH_3$ - $NH_4Cl$ buffer of pH 10·2 (0·5 ml) and a 2% soln. of dichlorobenzoquinonechlorimine in *iso*propyl alcohol (0·5 ml) and after 2 hr. measure the fluorescence in a Coleman fluorimeter with B-1 primary and P-C-1 secondary filters.
A. R. Rogers

3746. **Separation and colorimetric determination of *p*-aminobenzoic acid in procaine.** Shih-Jee Jow and Kuen Lung (Dept. of Pharm., Second Military Med. Coll., Shanghai). *Acta Pharm. Sinica*, 1959, **7** (1), 6–9.—*p*-Aminobenzoic acid (**I**) may be extracted satisfactorily with diethyl ether from aq. soln. of procaine at pH 3·6, K H tartrate being used as a buffer. The extract is evaporated to dryness and **I** in the residue is treated with 6 *N* acetic acid (5 ml) and 2% *p*-dimethylaminobenzaldehyde in ethanol (2 ml) (*cf.* Tanber, *J. Amer. Chem. Soc.*, 1941, **63**, 1488). The soln. is diluted to 25 ml with water and the yellow colour developed is measured after 1 hr. in a photometer at 458 mμ. The colour is stable for at least 1 week. Beer's law is obeyed in the range from 10 to 100 μg of **I**. S. H. Yuen

3747. **Separation and quantitative determination of phenylbutazone (4-*n*-butyl-1:2-diphenylpyrazolidine-3:5-dione) in pharmaceutical preparations.** M. Deffner and A. Issidorides-Deffner (Lab. de Contrôle et de Rech. de la Vitarine Greece Co., Cholargos-Athènes, Greece). *Chim. Anal.*, 1958, **40** (12), 460–462.—Phenylbutazone (**I**) gives a coloured complex with $FeCl_3$ and 2:2′-dipyridyl (**II**), which is measured spectrophotometrically. Treat 1 ml of test soln. (containing 0·25% of **I** in abs. ethanol) with 1 ml of 0·25% abs. ethanolic $FeCl_3.6H_2O$ (**III**) and 1 ml of 0·5% abs. ethanolic **II**. Make up to 25 ml with abs. ethanol and read the extinction at 520 mμ, 20 min. after the addition of **III**. A blank should be treated similarly and, as the extinction rises rapidly with time, and the rate falls off after 15 to 20 min., a known soln. should be similarly treated. The method is suitable for concn. of **I** from 5 to 30 μg per ml. For compressed tablets, several are powdered and a suitable aliquot is suspended in water and extracted with benzene, the extract being made up to a known vol. with benzene and an aliquot diluted with abs. ethanol to give 0·025% of **I**, and analysed as above. Similar extraction after acidification with HCl will give **I** combined as the Na or Ca salt. Results agree well with those by the B.P.C. gravimetric method, but results by measurement of the Na salt at 264 mμ are distinctly higher. Separation of **I** from other substances easily oxidised by $FeCl_3$ is achieved by chromatography, either on plain paper with butanol - water, or on paper treated with 50% formamide in acetone or 2·5% petroleum jelly in ether, with $CHCl_3$ or $CHCl_3$ - benzene as solvent, the spray reagent being a mixture of **III** and **II**, or Ehrlich reagent. R. E. Essery

3748. **Vanadametry. Assay of *iso*nicotinic acid hydrazide [isoniazid].** H. S. Gowda and G. G. Rao (Chem. Lab., Andhra Univ., Waltair, India). *Z. anal. Chem.*, 1959, **165** (1), 36–38 (in English).—Isoniazid (**I**) is rapidly and quant. oxidised by 0·05 *N* $Na_4V_2O_4$ in 8 *N* $H_2SO_4$ and may be determined by the back-titration of an added excess with standard $(NH_4)_2SO_4.FeSO_4$ soln. Excipients (lactose, glucose and starch) do not interfere. Results agree to within ±0·5% and 5%, respectively, with the results of bromimetric and iodimetric determinations of isoniazid and Rimifon tablets, respectively. *Procedure*—Weigh 20 tablets and crush finely. Dissolve a portion containing 0·3 to 0·4 g of **I** in water, filter, and dilute to 250 ml. To a 10-ml aliquot add 0·05 *N* $Na_4V_2O_4$ (20 ml) and 20 *N* $H_2SO_4$ (20 ml). After 1 min., back-titrate the excess of $Na_4V_2O_4$ with standard $(NH_4)_2SO_4.FeSO_4$ soln., with N-phenylanthranilic acid as indicator.
J. P. Stern

3749. **Determination of isoniazid methanesulphonate.** Masayoshi Tatsuzawa (Nat. Hygienic Lab., Tamagawa-yoga, Setagaya-ku, Tokyo). *Japan Analyst*, 1958, **7** (12), 790–792.—The oxidation titration of isoniazid methanesulphonate (**I**) with $KIO_3$ or $KBrO_3$ (*cf.* Kühni *et al.*, *Anal. Abstr.*, 1955, **2**, 1911) was examined with reference to the effect of starch, lactose and carboxymethylcellulose. The removal of $SO_2$ is completed by heating with dil. HCl for 5 min. There is no interference from the carbohydrates and formaldehyde produced by the hydrolysis of **I**. The sample (0·1 g) is dissolved in water (10 ml), boiled with 4 *N* HCl (10 ml) for 5 min., mixed with conc. HCl (20 ml) and 5 drops of 0·2% indigo carmine and titrated with 0·025 *N* $KIO_3$ or 0·1 *N* $KBrO_3$. K. Saito

3750. **Potentiometric determination of Artane [benzhexol] in non-aqueous solutions.** S. Negriţescu-Arizan. *Rev. Chim., Bucharest*, 1958, **9** (11), 627–629.—A differential titration method is used. First the free amine present as impurity is determined, and then the mixture of the benzhexol hydrochloride (**I**) with the Mannich base hydrochloride (**II**) (another impurity). *Procedure*—The sample (0·2 g) is dried at 105° and dissolved in warm glacial acetic acid (7 to 8 ml). After cooling it is titrated potentiometrically with $HClO_4$ (0·1 *N*) to the end-point (= *n* ml). To this soln. 4·3 ml of a soln. of mercuric acetate (5% in glacial acetic acid) is added, and the mixture is re-titrated. If *N* ml is the total titre, then (*N* − *n*) is the vol. (ml) of titrant equiv. to **I** plus **II**. A graph is used to determine the percentage of **I** in the mixture. It is claimed that the analysis requires only 30 min., and that errors do not exceed ±2%. H. Sher

3751. **Determination of phenolic compounds in pharmaceutical preparations using 4-aminophenazone.** C. A. Johnson and R. A. Savidge (Standards Dept., Boots Pure Drug Co. Ltd., Nottingham, England). *J. Pharm. Pharmacol.*, 1958, **10**, Supplement, 171T–181T.—Conditions affecting the method of determination of phenols based upon coupling with 4-aminophenazone in the presence of an alkaline oxidising agent have been examined and the importance of a rigid control of pH stressed. The

activity of many phenols of pharmaceutical terest has been investigated and the application the method to a number of pharmaceutical reparations is described. A. R. ROGERS

3752. **Complexometric determination of rivanol thacridine lactate**]. L. Przyborowski (Dept. of harm. Chem., Medical Acad., Lublin, Poland). *cta Polon. Pharm.*, 1959, **16** (1), 31–34.—An inrect complexometric method for the determination ethacridine lactate (**I**) is described, together with rocedures for commercial grades and pharmaceutal preparations. It is based on pptn. of **I** from an q. soln. with a standard soln. of $CdI_2$. The ppt. $(C_{15}H_{15}ON_3)_2H_2.CdI_4$ so formed is insol. in water ontaining KI. Excess of $CdI_2$ in the filtrate, uffered with hexamine, is determined complexoietrically, with xylenol orange as indicator. he method, which takes $<30$ min., is useful for atch determinations of substance, soln. and tablets. ilute aq. soln. of **I** used in medical prep. are best djusted to contain 0·05 to 0·2 g, and in tablets isually containing 0·1 g) the error is $\gtrsim 1\%$, after orrecting for the solubility of the ppt.
W. B. MIASKOWSKI

3753. **Methods for the determination of benzethonium chloride (Phemerol chloride).** D. M. Patel and R. A. Anderson (Parke, Davis & Co., Detroit, Mich., U.S.A.). *Drug Standards*, 1958, **26** (6), 189–193.—To a soln. of benzethonium hloride (300 mg) in $H_2O$ (75 ml) add 0·05% romophenol blue soln. (0·4 ml), $CHCl_3$ (10 ml) and N NaOH (1 ml) and titrate with 0·02 *M* Na tetrahenylboron, with shaking. The $CHCl_3$ layer hanges from blue to colourless at the end-point. The recovery in 8 replicate determinations ranged rom 100·1% to 100·4%. The following gravinetric procedure is of comparable accuracy and precision and may be applied to products that ontain a dye that interferes with the visual endoint of the titrimetric method. To a soln. of enzethonium chloride (150 mg) in 60% ethanol 50 ml) add 2·5% Na tetraphenylboron soln. (10 nl), with continuous gentle stirring, set aside vernight, filter through sintered glass, wash the ollected ppt. with $H_2O$ and weigh it after drying at 05° for 2 hr. A. R. ROGERS

3754. **Quantitative polarographic determination of 'Mercurit'.** N. Z. Bruja. *Rev. Chim., Bucharest*, 958, **9** (12), 685–688.—The method outlined for Mercurit' [the sodium salt of N-(3-hydroxymercuri-2-methoxypropyl)phthalamic acid] is claimed to be uitable for similar mercuric compounds. The nost suitable electrolyte is a mixture of 16 g of KCl and 12 g of citric acid per 100 ml; the pH should e between 3 and 5·5, when the value of $E_{\frac{1}{2}}$ becomes $-0{\cdot}35$ V. Oxygen must be removed by bubbling $CO_2$ through 10 ml of the test soln. for 5 min. *Procedure*—The 'Mercurit' soln. (0·0025 *M*) (1·4 ml) s treated with 38·6 ml of water and diluted to 00 ml with the basal electrolyte. A 5-ml aliquot s taken, O is removed and the polarographic letermination is carried out, the result being comared with a standard. The max. error is claimed o be $\pm 1\%$. H. SHER

3755. **Polarographic properties of nitro derivatives of 2-aminothiazole. I. Quantitative polarographic determination of 2-amino-5-nitrothiazole, and its acetyl and formyl derivatives.** A. Danek and M. Eckstein (Dept. of Inorg. and Anal. Chem., Med. Acad., Kraków). *Acta Polon. Pharm.*, 1959, **16** (1), 13–20.—2-Amino-5-nitrothiazole and its acetyl and formyl derivatives undergo reduction on the dropping mercury electrode in the presence of water - ethanol - KCl, giving 2-step reduction curves. The results show that all three preparations can be determined by this method at pH 1 to 12, and that for analytical purposes the application of buffer soln. is unnecessary as the curves are well developed in the ethanolic aq. soln. of KCl with the addition of gelatin. This method can be used for concn. of $\simeq 10^{-5}$ *M*. The height of the curves is linearly proportional to the concn. of the compound. The method can also be applied to the determination of 2-amino- and 2-acetamido-5-nitrothiazole in pharmaceutical preparations.
W. B. MIASKOWSKI

3756. **Isotope-labelled cancerostatic and bacteriostatic agents. I. Synthesis of [4:5-$^{14}$C]azauracil and [4-$^{14}$C]azathymine.** J. Morávek (Res. Inst. of Radiol., Prague). *Chem. Listy*, 1958, **52** (11), 2147–2152.—A radiochromatographic method has been found suitable for controlling intermediates and isolated products in the synthesis of 6-[4:5-$^{14}$C]-azauracil and 6-[4-$^{14}$C]-azathymine. The method has been carried out by a descending technique on Whatman No. 4 paper, with *n*-butanol saturated with $H_2O$ as solvent. The detection is by means of an apparatus in which the chromatograms are continuously passed across a Geiger - Müller tube and the activity is automatically registered. The use of various chemical detecting agents is described. The following compounds have been studied—oxalic acid ($R_F$ 0·0) (detection with bromocresol green), glyoxylic acid ($R_F$ 0·73) (detected with bromocresol green or dinitrophenylhydrazine), the thiosemicarbazone of glyoxylic acid ($R_F$ 0·59), thioazauracil ($R_F$ 0·61) (detected with u.v. light, with dinitrophenylhydrazine or $Ag_2CrO_4$), the thiosemicarbazone of pyruvic acid ($R_F$ 0·73), thioazathymine ($R_F$ 0·75) (detected in u.v. light with $Ag_2CrO_4$), and azathymine ($R_F$ 0·59). J. ZÝKA

3757. **Direct assay of fatty acid in the presence of its zinc salt in anti-fungal preparations.** D. E. Dean and R. I. Hackman (Anal. Development Lab., Shulton Inc., Clifton, N.J., U.S.A.). *Drug Standards*, 1958, **26** (6), 194–198.—The free acid is extracted with light petroleum and determined by non-aqueous titration. The results agree with those by the method of "New and Nonofficial Remedies," 1953 (Tests and Standards, p. 317), but are of much greater precision. *Procedure*—For a sample of anti-fungal powder, stir an amount containing $\simeq 0{\cdot}8$ milli-equiv. of free acid with light petroleum ($4 \times 15$ ml) in a sintered-glass funnel and filter under gentle suction. For a sample of anti-fungal ointment, mix an amount containing $\simeq 0{\cdot}8$ milliequiv. of free acid with $Na_2SO_4$ (2 g), shake with light petroleum ($3 \times 20$ ml) and centrifuge to effect separation of the phases. Dilute the combined extracts with acetone (60 ml) and titrate potentiometrically (antimony electrode and methanol-modified S.C.E.) with 0·1 *N* tetrabutylammonium hydroxide. Perform a control determination to compensate for the acidity of the acetone and for the $CO_2$ absorbed during the extraction.
A. R. ROGERS

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*See also Abstracts*—**3375**, Reagent for alkaloids. **3480**, Determination of Cr in sutures. **3556**, Determination of formyl and acetyl groups in digitalis glycosides. **3657**, Determination of colchicine. **3658**, Determination of phenylethylbiguanide. **3660**, **3661**, Determination of azovan

blue. **3676**, Determination of catechin in catechu. **3770**, Diastatic power of malt extract. **3805**, Precision in pharmaceutical analysis. **3806**, Measurement of density of liquids. **3823**, Chromatography of quaternary ammonium compounds. **3843**, Determination of prednisolone.

## Food

*Food and food additives, beverages, edible oils and fats, vitamins.*

3758. **Determination of the apparent purity of beet sugar factory juices and syrups. I.** W. H. Parker (British Sugar Corp., Ltd., 134 Piccadilly, London, England). *Int. Sugar J.*, 1958, **60** (720), 355–357.—The apparent purity of a juice or syrup is defined as the polarisation per 100° Brix. The sample (100 ml) is measured into a 100/110 ml flask and basic Pb acetate is added for clarification, the whole is made up to 110 ml, mixed and filtered, and the direct polarisation is taken in a 20-mm tube, a saccharimeter of 26 g normal weight being used. Then, if $S$ is the sugar (%), $P$ the polarisation, $B$ the ° Brix of the sample and $D$ its sp. gr., all at 20°, then $S = (0{\cdot}26 \times 1{\cdot}1 \times P)/(0{\cdot}99718 \times D)$, and purity $= 100S/B = 28{\cdot}6P/0{\cdot}99718BD$. Factors for the expression $28{\cdot}6/0{\cdot}99718BD$ can be calculated for various values of $B$, and then log purity = log $P$ + log factor. A slide-rule can then be constructed from which, given $P$ and $B$, the purity can be read. The construction of such a rule, 2 ft. long and covering the range 12° to 16° Brix, is described, purity being readable to 0·1%.
R. E. Essery

3759. **Studies on the determination of sugars in molasses, especially on the comparison of the Bertrand method and the Lane method, and the determination of unfermentable reducing sugars, varying the condition of inversion.** K. Okano and T. Kosaka. *Proc. Res. Soc. Japan Sugar Refineries' Technologists*, 1958, **7**, 51–64.—The two methods of analysis were investigated for soln. with different sugar and HCl concn., different inversion times or Pb acetate additions to sucrose soln. or molasses. Conclusions reached were—in sucrose soln. or molasses (each with 10% of sugars), nearly equal values for the reducing sugar content after inversion were obtained by either method, and the concn. of HCl or sugar did not affect the results; the use of lead clarifying agents, either before or after inversion, resulted in low values, the discrepancy being greater with larger amounts of lead reagent, and more with the Bertrand method than with the Lane method; the results with inverted molasses were irregular, soln. with $\simeq$25% of sugar showed the highest reducing values, and the Bertrand method gave higher figures. With larger amounts of HCl for inversion, more unfermentable sugars seemed to be produced. Sugar Ind. Abstr.

3760. **Simplified method of protein determination in cereals and cereal products.** J. Janicki, E. Kaminski and R. Ozog (Inst. für Getreideforsch., Warszawa, Poland). *Getreide*, 1958, **8** (12), 89–90.—The use of boiling-tubes, instead of flasks, for Kjeldahl digestions is described. These are held in a specially designed duralumin block which is heated either electrically or by gas. In the distillation process the ammonia is distilled into 2% boric acid and titrated directly, with a mixture (5:1) of bromocresol green and methyl red as indicator.
J. V. Russo

3761. **Estimation of the total solids and solids-not-fat of milk from the density and fat content.** S. J. Rowland and A. W. Wagstaff (Nat. Inst. Res. Dairying, Shinfield, Reading, England). *J. Dairy Res.*, 1959, **26** (1), 83–87.—The accuracy of the method specified in British Standard 734:1937 is assessed on 2425 samples (in five series over different years) against the gravimetric method. The percentages of solids by the density method were lower by an average of 0·06 than those determined gravimetrically. To correct for this error and to compensate for the lower, more accurate fat percentages arising from the recent reduction in the Gerber milk pipette, the following modified formulae are proposed—$T = 0{\cdot}25D + 1{\cdot}22F + 0{\cdot}72$, and S.N.F. $= 0{\cdot}25D + 0{\cdot}22F + 0{\cdot}72$. These formulae were adopted in October 1957, in an amendment to the B.S. 734 published in 1955. W. H. C. Shaw

3762. **Direct determination of citric acid in milk with an improved pyridine - acetic anhydride method.** J. R. Marier and M. Boulet (Nat. Res. Council, Ottawa, Canada). *J. Dairy Sci.*, 1958, **41** (12), 1683–1692.—A study is made of the reaction conditions at temp. from 17° to 60°. The recommended method can be applied directly to diluted milk (after centrifuging or diluting and filtering), to milk serum and, with a correction for interference by fat, to homogenised milk. A correction is also required if trichloroacetic acid is used in preparing the serum. *Procedure*—To 1·0 ml of sample containing 25 to 200 $\mu$g of anhydrous citric acid add 1·30 ml of pyridine. Swirl briskly, add 5·70 ml of acetic anhydride, swirl again and place in a water bath at 32° $\pm$ 0·25°. After 30 min. cool and measure the extinction at 420 m$\mu$ within 30 min. against a blank prepared with 1·0 ml of water instead of the sample. The curve is rectilinear up to 200 $\mu$g of citric acid.
W. H. C. Shaw

3763. **Colorimetric determination of available lysine in milk.** Susumu Adachi and Takeo Nakanishi (Fac. of Agric., Tohoku Univ., Kitaku-bancho, Sendai). *J. Agric. Chem. Soc. Japan*, 1958, **32** (9), 728–732.—The reaction between the $\epsilon$-amino group of lysine and 1-fluoro-2:4-dinitrobenzene (**I**) (Carpenter and Ellinger, *Biochem. J.*, 1955, **61**, xi) was applied to the determination of lysine. The extinction of $\epsilon$-dinitrophenylated lysine (**II**) at 455 m$\mu$ is proportional to the concn. for $<$3 mg of the hydrated hydrochloride of **II** per 100 ml. On extraction with diethyl ether, **II** remains in the aq. phase with other dinitrophenylated products. *Procedure*—Dissolve $NaHCO_3$ (100 mg) in the sample of milk (0·5 ml), add **I** in ethanol (2·5%) (2 ml) and set aside in the dark for 2 hr. Expel the ethanol, add HCl (6 *N*) (5 ml), seal the tube and keep at 105° for 15 min. Filter the product, dilute to 10 ml and shake a 2-ml aliquot with ether (2 $\times$ 10 ml). To 1 ml of the aq. layer add 5% acetic acid (0·7 ml) and *N* NaOH (2·7 ml) to adjust the pH to 4·5, make up to 10 ml and measure the extinction. K. Saito

3764. **Reaction of lactose with anthrone and its application to the estimation of lactose in casein and other dairy products.** E. L. Richards (Dairy Res. Inst., Palmerston North, New Zealand). *J. Dairy Res.*, 1959, **26** (1), 53–57.—For the rapid and accurate determination of lactose in casein a modification of the anthrone reaction is recommended. *Reagent*—Dissolve 150 mg of anthrone in 70% v/v $H_2SO_4$ (98% w/w) to 100 ml. Cool and store for $\lt$2 hr. (preferably overnight) at 0°. *Procedure*—Place

casein and 0·1 g of $NaHCO_3$ in a large boiling-
Add 25 ml of water, warm and stir in a bath
to 70° until the casein has dissolved (10 to 15
Add with stirring 25 ml of 0·1 *N* $H_2SO_4$ and
Place 1 ml of filtrate (> 100 μg of lactose)
boiling-tube immersed in an ice bath. Add,
shaking, 10 ml of ice-cold anthrone reagent.
er the tube, mix and place in a boiling-water
for 6 min. Cool in an ice bath for 30 min.
read the extinction at 625 mμ. Use 1 ml of
for the blank and calibrate by including a
lard (100 μg) with each batch of analyses
curve is rectilinear. For milk, dilute 1 ml of
le to 500 ml with water and take 1 ml for assay.
W. H. C. Shaw

65. **Determination of NN′-diphenyl-*p*-phenylene-ine (DPPD) in milk by paper chromatography.** .. Dehority (Storrs Agric. Exp. Sta., Conn., A.). *J. Chromatography*, 1959, **2** (1), 81–83.—difficulty arising in the determination of diphenyl-*p*-phenylenediamine (**I**) in milk to the insolubility of part of the non-saponie fraction in an acetone - $HNO_3$ mixture can be come by paper chromatography. Soln. of **I** enzene are chromatographed with 80% aq. anol. A band between $R_F$ 0·70 and 0·85 is cut nd shaken with conc. $HNO_3$, and the extinction 90 mμ is measured. With pure benzene soln. the recovery is 95·8%. Recovery of **I** added to before the extraction of the non-saponifiable ion is 51·44% ± 3·85 (8 determinations).
G. Burger

66. **Detection of butylated hydroxytoluene in** J. Wurziger and R. Pohlmann (Chem. u. nsmitteluntersuchungsanst., Hygien. Inst., burg). *Dtsch. LebensmittRdsch.*, 1958, **54** (12), 308.—The method is based on the production her-soluble coloured substances when butylated roxytoluene (**I**) is treated with ethanolic KOH owdered $Ca(OH)_2$. These coloured compounds v a strong and sharp absorption maximum at mμ. *Procedure*—Lard (5 g) is saponified for nin. with 25 ml of *N* ethanolic KOH. Water ml) is added and the mixture extracted with nyl ether (2 × 50 ml). The ether soln. is ned with water (3 × 10 ml), dried with anhyd. $SO_4$ for 15 min., and evaporated. The residual ponifiable material is then heated with 10 ml ethanolic KOH for 10 min. on a boiling-water . On cooling, a red to tan colour appears in presence of **I**. The method will detect 0·005% (0·25 mg in 5 g of lard), and can be made nt. by comparison with standards similarly ed. Gallates, nordihydroguaiaretic acid, butyl-hydroxyanisole and fat oxidation products do interfere, as the coloured compounds formed n these are insoluble in ether. E. C. Apling

67. **Determination of sugars in fruits. I. t of conditions of hydrolysis on the determina- of sucrose.** Kazuo Osodo, Hidejiro Kazumi, yuki Kotaka and Hanao Shitomi (Instruction of Rural Ind., Numata, Shinjo, Yamagata-. *J. Agric. Chem. Soc. Japan*, 1958, **32** (9), 673.—For the hydrolysis of sucrose in fruits aining 60 to 70% of fructose in the total sugar, ollowing conditions were suitable—0·1% HCl, 30 min. in a boiling-water bath; 2·4% HCl, 16 hr. at 30°, or 4 to 8 hr. at 40°, or 45 to 60 min. 0°. No appreciable decomposition of fructose observed. The determination of invert sugar effected by Somogyi's method (*J. Biol. Chem.*, **100**, 695). K. Saito

3768. **Determination of *o*-hydroxydiphenyl in oranges.** W. Thole (Bundesgesundheitsamt, Max von Pettenkofer Inst., Abt. f. Physiol., Pharmakol. u. Arzneimittelwesen, Berlin-Dahlem, Germany). *Z. LebensmittUntersuch.*, 1959, **109**, 40–43.—*Procedure*—Mix the sample (200 g) with water (500 ml) and $H_3PO_4$ (5 ml), and steam-distil into a receiver containing 500 ml of water. Extract the distillate (1 litre) with *cyclo*hexane (3 × 50 ml). Extract the preservative from the *cyclo*hexane into 0·1 *N* NaOH (10 × 15 ml), make up the extracts to 150 ml with 0·1 *N* NaOH, and (within 1 hr.) make up 20 ml of the soln. with a borate buffer at pH 10·4 (3·15 ml) and 0·1 *N* NaOH to 50 ml. To this soln. add (without delay) a 2% aq. soln. of 4-aminophenazone (0·5 ml) and 2% aq. $K_3Fe(CN)_6$ (1 ml), and measure the colour at 510 to 520 mμ in comparison with the colour obtained from standard soln. of the preservative. Maximum errors are +3% and −7%.
P. S. Arup

3769. **Phenolic constituents of *Prunus domestica*. I. The quantitative analysis of phenolic constituents.** T. Swain and W. E. Hillis (Div. of Forest Products, C.S.I.R.O., Melbourne, Australia). *J. Sci. Food Agric.*, 1959, **10** (1), 63–68.—Gum in the flesh of canned plums may be related to the transport of phenolic glycosides from the kernels; methods for determining these are discussed. *Total phenols*—Dilute an aliquot of sample soln. (containing > 0·5 ml of alcohol) with $H_2O$ to 7 ml in a 10-ml tube. Add 0·5 ml of Folin - Denis reagent and shake. Add 1 ml of satd. $Na_2CO_3$ soln. 3 min. later, and dilute to 10 ml. Measure the extinction at 725 mμ after 1 hr. against a $H_2O$ - reagent blank. *Leucoanthocyanins*—Place 1 ml of sample soln. (> 50% of alcohol) in each of two tubes (6 in. × 1 in.) and add 10 ml of reagent (25 ml of conc. HCl diluted to 500 ml with *n*-butanol). Shake and place one tube in a water bath at 97° ± 1°. After 3 min., stopper the tube and heat for a further 37 min.; remove the stopper and cool the tube in $H_2O$ for 5 min. Measure the extinction at 550 mμ (also at 650 mμ if chlorophyll is present) against the contents of the unheated tube. *Flavanols*—Place aliquots (containing > 0·1 ml of methanol) in two 25-ml flasks, *A* and *B*. Add 4 ml of fresh reagent (1% vanillin in 70% v/v $H_2SO_4$) to *A* and 4 ml of 70% $H_2SO_4$ to *B*, keeping the temp. > 35°. After 15 min. measure the extinctions of *A*, *B* and a blank *C* (4 ml of reagent plus 2 ml of $H_2O$) at 500 mμ against 47% $H_2SO_4$. Subtract readings for (*B* + *C*) from *A*. *Anthocyanins*—Place 3 ml of HCl (0·5 *N* in 80 to 85% v/v methanol) in each of 2 tubes. Dilute one with 1 ml of HCl in methanol (5 : 1 v/v, 3 *N*) and add 1 ml of reagent (1 ml of 30% $H_2O_2$ in 9 ml of 3 *N* HCl in methanol, 5 : 1 v/v) to the tube containing the sample. Set aside in the dark for 15 min. and measure the extinction at 525 mμ, with the first tube as a blank. P. D. Parr-Richard

3770. **Determination of the diastatic power of malt and malt extract.** S. Gerardis. *Birra e Malto*, 1958, Nov., 24–28.—A method slightly modified from that of Pollak and Egloffstein is recommended. Test extracts of malts were prepared by extracting 10 g of finely ground malt (or 5 g of malts of high diastatic power) with 160 ml of water at 40° for 30 min., then cooling to 18° to 20°, making up to 200 ml and filtering. Malt extract (10 g) was dissolved in warm water and the soln. cooled to 18° to 20° and made up to 200 ml. Starch paste for conversion was prepared fresh daily by stirring a slurry of 9 g of arrowroot starch (10 to 15% of

moisture) in a little water into 250 ml of water at 90° to 95°. After being stirred at this temp. for 30 min., the paste was cooled to 18° to 20° and made up to 300 ml; 50 ml was removed and 3 ml of acetate buffer (pH 4·7) was added to the remaining 250 ml. For saccharification, 250 ml of the buffered starch paste was incubated with 4 ml of test extract at 37·6° for precisely 30 min., when the reaction was stopped by the addition of 10% KOH soln. (3 ml). The mixture was cooled to 18° to 20° and made up to 300 ml. The maltose content of this conversion liquid was determined by titration with Fehling's soln. (5 ml each of reagents *A* and *B*, diluted with 60 ml of water). Results were calculated as indicated by Muntoni (*J. Inst. Brew.*, 1958, 431).

ABSTR. J. INST. BREW.

3771. **Paper-chromatographic determination of L(+)-ascorbic acid in beer.** H. R. Stocker. *Schweiz. Brauerei Rdsch.*, 1958, **69** (12), 211–213.—Ascorbic acid (**I**) can be separated from other reducing substances with *n*-butanol - water - acetic acid (4:1:1) as ascending solvent, in an atmosphere previously saturated with the solvent vapour, and located by spraying with 2:6-dichlorophenolindophenol (**II**) in 50% ethanol. The requisite amount of test sample may reach 0·4 ml. A soln. of **I** in aq. 0·5% metaphosphoric acid is used as a standard for comparison in parallel runs. The corresponding unsprayed spots are cut out and eluted with 3% aq. oxalic acid, 1 to 5% aq. metaphosphoric acid, or methanol. The determination can be made by titration of the eluate with 0·001 *N* **II**, or (preferably) by spectrophotometric measurement of the coloration produced on admixture with a soln. of **II** under specified conditions. P. S. ARUP

3772. **Determination of the humulone of hops by conductimetric titration.** J. de Clerck and J. Jerumanis. *Bull. Ass. Éc. Brass., Louvain*, 1958, **54**, 249–253.—Extraction of hops by means of hexane before conductimetric titration as recommended by Hartong *et al.* (*Int. Tijdschr. Brouw. Mout.*, 1956–1957, 15) yields low results. In the present method, extraction is effected in a blender with methanol, and the resins are transferred to hexane as in the gravimetric Walker-Hastings determination as modified by de Clerck (*Cours de Brasserie*, Van Linthout, Louvain, 1948, Vol. 2, p. 210). The humulone is then determined by conductimetric titration. An aliquot (100 ml) of the hexane soln. is concentrated to 10 ml, methanol (20 ml) is added and the soln. is washed into a conductivity cell with methanol (2 × 10 ml). The soln. is titrated with 4% Pb acetate soln., and the required vol. of this soln. multiplied by a factor of 1·524 gives the percentage of humulone in the hops. The precision of the method compares favourably with that of the gravimetric method in the analysis of hops containing 4 to 7% of humulone, and is superior in the analysis of old hops containing <1·5% of humulone. ABSTR. J. INST. BREW.

3773. **Determination of tartaric acid in wine.** W. Diemair and G. Weinberger (Univ. Inst. f. Lebensmittelchem., Frankfurt a. Main, Germany). *Z. Lebensmitt Untersuch.*, 1959, **109** (1), 34–40.—The accuracy of the micro-method of Gorbach and Vaupotitsch (*cf. Anal. Abstr.*, 1957, **4**, 3130) decreases considerably as the amount of tartaric acid present in the sample falls below 100 mg per litre. In such cases the results are greatly influenced by the amount of washing undergone by the pptd. K H tartrate. P. S. ARUP

3774. **Paper-chromatographic studies on fa** M. Jáky (Forschungsinst. f. Pflanzliche Ö Budapest). *Fette, Seif., Anstrichmitt.*, 1959, (1), 6–10.—The $R_F$ values of fatty acids were det mined by the chromatography of known mixtur and used in the analysis of fatty acid mixtur from the seed oils of sunflower, poppy, cotton a maize. The separated acids were quant. det mined by a micro-titration procedure, which described. In all cases considerable amounts linoleic acid were present in addition to oleic ac Monoglycerides have been separated by eluti with acetone and developing the spots with a 0·05 aq. soln. of Rhodamine B (C.I. Basic Violet 10), a quant. determined by measuring the size of t spots. Results are satisfactory and the determin tion can be completed in ≃2 hr. Unsaponifiab material can be analysed by chromatographing 1% soln. of the extracted fraction in light petroleu (boiling-range 190° to 210°), eluting with ethano *iso*propyl alcohol - water (20:2:3) satd. with lig petroleum, and developing with Rhodamine B $KMnO_4$ soln. α-Tocopherol is present in all t oils examined, and other tocopherols and ster have also been identified. Results are tabulate By eluting in several stages, separation of a neutr oil containing triglycerides into 4 fractions w achieved. The fractions were then saponified a the fatty acid mixtures chromatographed. T linolein and glycerides of oleic and linoleic aci have been shown to be present in sunflower-seed o and glycerides of erucic and stearic acids in rap seed oil. S. M. MARSH

3775. **Revision of "Standard testing methods f the fats and waxes industry". XXVIII. Analys of waxes and wax products.** A. Seher and G. v Rosenberg (Dtsch. Inst. f. Fettforschung, Uni Münster, Westfalen). *Fette, Seif., Anstrichmitt* 1959, **61** (1), 17–20.—This is Report No. 38 collaborative work undertaken under the auspic of the Deutsche Gesellschaft für Fettwissenschaf Full details, with diagrams of apparatus, are give for the recommended procedures for sampling, a the determination of alkali number, water conten and normal paraffin content of waxes. A metho is also given for the determination of acetone-solub matter in montan wax. S. M. MARSH

3776. **Colorimetric determination of urease activit in soya-bean oil.** G. Schramm and P. D. Aine (Procter & Gamble Co., Cincinnati, Ohio, U.S.A. *J. Amer. Oil Chem. Soc.*, 1959, **36** (1), 1–3.—To 1 of meal is added 50 ml of a urea soln. (0·4 ± 0·0005 of urea dissolved in 1 litre of a buffer soln. prepare from 22·3 g of $Na_4P_2O_7.10H_2O$ in 980 ml of wat and 3 ml of HCl; the pH is adjusted to 7·7 to 7·8 and the mixture is heated at 40° for 30 min., wit shaking every 5 min. The soln. is then remove from the source of heat and 0·5 ml each of con HCl, ferrocyanide soln. [10·6 g of $K_4Fe(CN)_6.3H_2$ dissolved in 100 ml of water] and Zn acetate sol (22 g of Zn acetate dihydrate dissolved in 3 ml acetic acid and 100 ml of water) and 0·1 g of cha coal are added. After shaking for 15 min. the sol is filtered, and 10 ml is diluted to 25 ml wit water; 10 ml of this soln. is mixed with 10 ml *p*-dimethylaminobenzaldehyde soln. (16 g in 1 lit of 95% ethanol and 100 ml of conc. HCl), and aft shaking the mixture for 10 min. the extinctions the test soln. and a reagent blank are measured 430 mμ. The concn. of urea is determined b comparison with a standard curve, and the urea

ity is expressed as the amount of urea decomposed under the specified conditions.

G. R. Whalley

77. **Paper chromatography of fats. XXIX. Quantitative analysis of fatty acid mixtures by use of the copper - mercury process.** H. P. Kaufmann and H. Schnurbusch (Inst. f. Pharm. u. Lebensmittelchem., Univ. Münster, Germany). *Fette, Seif., Anstrichmitt.*, 1958, **60** (11), 1046–1050. Saturated and unsaturated fatty acids and their esters can be determined by quantitative paper chromatography if undecane (*cf.* Kaufmann and Schnurbusch, *Ibid.*, 1958, **60**, 165) is used as the stationary phase. The dried chromatograms are treated for 1 hr. with 2% mercuric acetate in 1% v/v acetic acid and washed for 4 hr. in $H_2O$. The dried chromatograms are sprayed with 0·1% ethanolic diphenylcarbazone. Artificial mixtures of arachidic, behenic, palmitic, myristic and lauric acids were analysed, determined by the copper and above-described mercury methods using planimetry. Results by both methods agreed well. Good agreement was also obtained with a mixture of oleic, linoleic and linolenic acids. As $Hg^{2+}$ react with the double bond and the carboxyl group and copper only with the latter, a combination of the two methods is suggested for the quant. separation of critical pairs (*e.g.*, linoleic and myristic acids). A formula for the calculation of the composition of such a mixture is given. Results for the analysis of the fatty acid content of a number of natural fats by the combined methods are given.

S. Baar

778. **Analysis of long-chain fatty acids by gas - liquid chromatography. Micro-method for preparation of methyl esters.** W. Stoffel, F. Chu and E. H. Ahrens, jun. (Rockefeller Inst., 66th Street and York Avenue, New York, U.S.A.). *Anal. Chem.*, 1959, **31** (2), 307–308.—The following method for the preparation and isolation of the methyl esters from lipid mixtures eliminates the use of alkali and diazomethane, which may lead to isomerisation and oxazoline formation. *Procedure*—Heat the esters (5–10 mg) with dry benzene (0·5 ml) and a 5% soln. of HCl in super-dry methanol (4 ml) under reflux at 75° to 100° for 2 hr. with shaking. Cool, add $H_2O$ (1 ml) and extract with light petroleum (boiling-range 30° to 36°) (3 × 3 ml). Neutralise and dry the extracts over $Na_2SO_4$ - $NaHCO_3$ (4:1) for 1 hr. Finally evaporate to dryness at 40° under reduced pressure. Purify the residue by sublimation at 60° to 80° at a pressure of 0·2 mm (Hg) for 1 hr.

A. R. Rogers

779. **Detection of certain brominated long-chain fatty acid esters by gas - liquid chromatography.** A. Landowne and S. R. Lipsky (Yale Univ. School of Med., New Haven, Conn., U.S.A.). *Nature*, 1958, **182**, 1731–1732.—Chromatography of a brominated mixture of methyl stearate and methyl oleate (1:2) on an 8-ft. column of 60 to 80-mesh Celite 545 coated with 10% poly(diethylene glycol adipate) at 205°, with argon as carrier gas, revealed the presence of three peaks in addition to that of unchanged stearate. The retention volumes of the new components, which are unidentified, are greater than those of the original esters.

A. R. Rogers

780. **Enzymatic determination of polyunsaturated fatty acids.** J. MacGee (Miami Valley Lab., Procter & Gamble Co., Cincinnati, Ohio, U.S.A.). *Anal. Chem.*, 1959, **31** (2), 298–302.—A rapid method for the quant. determination of total *cis*-methylene-interrupted polyene acids is described. As little as 5 $\mu$g of linoleic acid can be determined with good accuracy; the coeff. of variation for 20 determinations of the extinction coeff. of linoleic acid was 1·8%. *Procedure*—Prepare a soln. of the sample in 0·2 *M* borate buffer of pH 9·0; esters must first be hydrolysed. Mix a 0·02% soln. of lipoxidase in 0·2 *M* buffer (0·1 ml) with a 3-ml aliquot, containing between 5 and 25 $\mu$g of free polyunsaturated fatty acids. Set aside at room temp. for 30 min. and measure the extinction at 234 m$\mu$ against a blank soln. prepared similarly but with use of boiled enzyme. The method has been applied to fats, oils, hydrogenated fats, fatty acids, esters, blood plasma, micro-organisms and plant seeds.

A. R. Rogers

3781. **Gas - liquid chromatography of highly unsaturated fatty acid methyl esters.** W. Stoffel, W. Insall, jun., and E. H. Ahrens, jun. (Rockefeller Inst., New York, U.S.A.). *Proc. Soc. Exp. Biol. Med.*, 1958, **99** (1), 238–241.—Gas - liquid chromatography was carried out as described by James and Martin (*Biochem. J.*, 1956, **63**, 144) with an ionisation chamber detection method (*cf.* Lovelock, *Anal. Abstr.*, 1958, **5**, 3208), with the chamber vapour-jacketed at 197°. *Procedure*—Supply the mobile phase (argon) at a pressure of 170 mm (Hg). Pack each 4-ft. column with 5 g of acid-washed alkali-treated Celite 545 (140 to 200 mesh). Two stationary phases were studied, the non-polar vacuum grease Apiezon M and the polar polyester Reoplex 400. The Apiezon column contains 0·8 g of Apiezon and the Reoplex column 2 g of Reoplex 400. Condition both columns at 197° by flushing with N at 670 mm (Hg) for at least 3 days before analytical use. Calculate all relative retention volumes from apparent retention times (= time from the air peak to centre of the symmetrical elution peak). Recover the esters after chromatography by leading the effluent gas from the detector into a glass tube loosely packed with defatted cotton moistened with abs. ethanol. Proof is given that methyl esters of highly unsaturated long-chain fatty acids are not significantly altered in chemical structure during gas - liquid chromatography under the conditions given.

B. P. Block

3782. **Improved iodimetric methods for the determination of lipid peroxides.** F. W. Heaton and N. Uri (Min. of Agric., Fisheries and Food Res. Estab., Greyhope Road, Aberdeen). *J. Sci. Food Agric.*, 1958, **9** (12), 781–786.—By de-aerating the test soln., errors due to induced oxidation are reduced; special reaction vessels are described. For the macro-procedure, take a sample containing $\leqslant 5$ $\mu$moles of peroxide, add 70 ml of a 2:1 mixture of glacial acetic acid and $CHCl_3$ and de-aerate continuously with pure N; follow the usual procedure and titrate with 0·002 *N* $Na_2S_2O_3$. The standard deviation is $\pm 0{\cdot}087$ (4 determinations). For samples containing 0·02 to 5 $\mu$moles, use 7·5 ml of de-aerated solvent; the total vol. including the KI soln. should be $\geqslant 10$ ml. Measure the absorption at 370 to 500 m$\mu$ according to concn. (400 m$\mu$ for the concn. range 0·1 to 1·2 $\mu$mole of peroxide), excluding O throughout the test. The peroxide concn. can be determined in terms of either hydroperoxide or iodine by reference to the appropriate calibration curve.

P. D. Parr-Richard

3783. **Analytical detection of synthetic antioxidants in edible fats.** A. Seher (Dtsch. Inst. f. Fettforschung, Münster, Westf., Germany). *Fette, Seif., Anstrichmitt.*, 1958, **60** (12), 1144–1153.—Tabulated results of the application of seven tests for the presence of 20 antioxidants in fat show the necessity for the application of at least three of the tests, namely the reactions with molybdophosphoric acid, ferric thiocyanate and ferric ferricyanide. Positive results are obtained with autoxidised oils (of peroxide value $<10$) in the absence of any antioxidant; negative results are, however, obtained after the removal of peroxides. Autoxidation products showing peroxide values $>6$ can similarly interfere with the determination of antioxidants by titration with ceric sulphate. When applying the Amer. Oil Chem. Soc. stability test to arachis oil, the time of heating at 105° should be prolonged to 8 hr. Spectrophotometric data are given for 10 antioxidants. For the isolation of antioxidants for spectrophotometric analysis, it is recommended to extract a soln. of the sample (20 g) in hexane (40 ml) with 75% methanol (2 × 30 ml), all operations being carried out in a current of inert gas.

P. S. Arup

3784. **Photometric determination of vitamin D in presence of vitamin A.** M. Schmall, B. Senkowski, R. Colarusso, E. G. Wollish and E. G. E. Shafer (Anal. Res. Lab., Hofmann-La Roche Inc., Nutley, N.J., U.S.A.). *J. Amer. Pharm. Ass., Sci. Ed.*, 1958, **47** (12), 839–844.—A basic method and three modifications are presented. Recovery experiments and a comparison of results with those obtained by bio-assay suggests that the method is accurate to about ±5%. *Procedure*—Saponify the sample, containing 4000 i.u. of vitamin D (**I**), and extract the unsaponifiable matter with light petroleum (boiling-range 30° to 60°). Transfer an aliquot to a column of Florex XXS and elute **I** with benzene. Carefully evaporate the eluate to dryness and dissolve the residue in $CHCl_3$. Allow an aliquot to react with the $SbCl_3$ reagent of Mulder *et al.* (*cf. Anal. Abstr.*, 1958, **5**, 998). Correct the extinction at 495 mμ by use of the colour inhibitor and method of calculation of Wilkie *et al.* (*cf. Anal. Abstr.*, 1959, **6**, 1538). Simultaneously perform a control determination of a known amount of **I** to which have been added vitamin A (**II**) and vitamin E in about the same amounts as are contained in the sample. For low-potency samples when interference is encountered with the basic method, mix the sample with water, saturate the soln. with crystalline sodium sulphate, extract with light petroleum, evaporate the extracts to dryness and apply the basic procedure to the residue. Alternatively, saponify, extract and purify on a column of Florex by the basic procedure, evaporate the benzene eluate to dryness, and apply a soln. of the residue in light petroleum to a column of $Al_2O_3$ containing 8% of water; remove degradation products of **II** by elution with benzene - light petroleum (3 : 1), then elute **I** with benzene and carry out the basic colorimetric procedure. For samples which contain a high proportion of **II**, saponify an amount of sample containing ≃7500 i.u. of **I**, and dissolve the unsaponifiable matter in the upper phase of a mixture of butanol - methanol - water - heptane (1 : 3 : 2 : 4). Apply the solution to a column of Hyfax polyethylene powder and develop with the lower phase of the solvent mixture. Remove the upper part of the column, which contains the **I**, and extract it with light petroleum. Then proceed with the chromatographic purification on Florex and colorimetry by the basic procedure. A. R. Rogers

3785. **Studies on the microbiological assay vitamins and amino acids by the pulp-disc metho I; II. The assay of several vitamins of the B grou** Hisao Ogawa, Yutaka Matsuya, Hiroko Ozaw Makoto Kondo and Teijiro Uemura (Fac. of Agri Tohoku Univ., Kitaroku-bancho, Sendai). *J. Agr Chem. Soc. Japan*, 1958, **32** (1), 33–42.—The use a sulphite pulp disc in place of a cup-plate w studied with biotin (**I**), pantothenic acid (**II** nicotinic acid (**III**) (with *Lb. arabinosus* 17–5 pyridoxine (**IV**) (with *Sacch. carlsbergensis* ATC 4228), and thiamine (**V**) (with yeast) (Sato *et a Ibid.*, 1957, **31**, 675). A sulphite pulp disc (dia 11 mm) is impregnated with the sample sol (0·05 ml), placed on Snell's medium (for **I**, **II** a **III**) (*J. Biol. Chem.*, 1941, **139**, 675) or Atkin's ag (1%) medium (for **IV** and **V**) (*Ind. Eng. Chem Anal. Ed.*, 1943, **15**, 141), incubated at 37° for 12 h (for **I**, **II** and **III**) or at 30° for 14 hr. (for **IV** and and the diameter of the colony measured. The l of the concn. $c$ the diameter for 5 to 500 μg of per ml, 0·5 to 50 μg of **II** and **III** and 0·05 to 5 of **IV** and **V**. The sensitivity is lower than the tes tube method but the variation (<5%) is les The sterilised culture can be preserved for sever weeks. No interference results from <20% NaCl or $Na_2SO_4$.

**III. Application to some vitamins and ami acids.** Hisao Kojima and Yutaka Matsuy *Ibid.*, 1958, **32** (2), 100–105.—This method w applied to 11 other vitamins and 18 amino aci with various bacilli and yeasts. Folic acid (0·01 1 μg per ml) and riboflavine are determined wi *Lb. casei*, inositol (10 to 1000 μg) with *Sacc carlsbergensis* and vitamin $B_{12}$ (0·01 to 0·5 μg) wi *Lb. leichmannii*. DL-α-Alanine (100 to 1000 per ml) is determined with *Lb. citrovorum*, arginine, DL-aspartic acid, L-cystine (25 to 25 μg), L-glutamic acid, glycine (25 to 2500 μ L-histidine, L-lysine, DL-methionine, L-proline, D serine and DL-threonine (50 to 5000 μg each) a determined with *Leuc. mesenteroides*, and D *iso*leucine, L-leucine, DL-phenylalanine, DL-trypt phan (25 to 2500 μg), L-tyrosine (25 to 2500 μ L-glutamic acid and DL-valine (50 to 5000 μg eac with *Lb. arabinosus*.

**IV. Examination of the determination of ami acids.** Hisao Kojima and Yutaka Matsuy *Ibid.*, 1958, **32** (2), 106–110.—Determination L-lysine, DL-methionine (with *Leuc. mesenteroide* L-glutamic acid and DL-phenylalanine (*Lb. ara nosus*) was carried out with various samples. T variation is <10% and no interference results fro <20% of NaCl. Substances affecting the diffusi of the amino acid interfere.

**V. Attempts to decrease the time for determinatio** Hisao Kojima and Yutaka Matsuya. *Ibid.*, 19 **32** (3), 189–192.—The time taken for the develo ment of the colony decreases with increasing conc of the incubated micro-organism, but the bounda becomes less distinct with prolonged cultivatio By the use of 1% *Sacch. carlsbergensis* or *L arabinosus*, 10 hours' culture suffices. The ag concn. has little effect on the result. K. Saito

3786. **Spectrophotometric determination of py doxal-5-phosphate.** V. Bonavita and V. Sca (Inst. of Human Physiol., Univ. of Naples, Ital *Anal. Chim. Acta*, 1959, **20** (1), 47–50.—Pyridoxal-phosphate (**I**) is determined by measuring the chan in the u.v. absorption spectrum which occurs af treatment with KCN at pH 7·4. *Procedure*— the sample (3 ml containing <75 μg of **I**) add K

(0·1 ml, 0·03 *M* in 0·2 *M* phosphate buffer). at 50° for 45 min. and compare the extinction 35 mμ with a similar sample containing phose buffer only. The difference is referred to a ration curve. The method is specific and much tedious than enzymic methods.

W. T. Carter

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*e also Abstracts*—**3667**, Determination of vita- $B_{12}$. **3705**, Determination of iodine in foods. , Determination of nicotinic acid. **3802**, rmination of nicotinic acid in feeding-stuffs.

## Sanitation

*Analysis of air, water, sewage, industrial wastes, industrial poisons.*

87. **Comparative phenolic spot tests. Applicato some air particulate fractions.** G. E. Inglett J. P. Lodge (U.S. Public Health Service, Cinati, Ohio). *Anal. Chem.*, 1959, **31** (2), 248–249. mparative spot tests in which four different ents were used (diazotised sulphanilic acid, aldehyde - $H_2SO_4$, Millon's reagent and 4- iophenazone) were applied to 34 phenols and haracteristic colours and lower detection limits determined. The tests were applied to the acid fractions of the benzene-soluble particumatter from 11 U.S. cities. Samples from two cated the presence of phenolic compounds. lence was obtained for the presence of flavonpresumably derived from pollen in the samples.

G. P. Cook

88. **Determination of small quantities of ozone om air.** G. A. Hunold and W. Pietrulla (Lab. hem. Toxikol., Bundesgesundheitsamt, Berlinlem). *Z. anal. Chem.*, 1959, **165** (1), 20–28.— method of Deckert (*cf. Anal. Abstr.*, 1957, **4**, , in which paper impregnated with $Fe(SCN)_3$ ed, is unsuitable for the quant. determination ·001 to 0·2 mg of $O_3$ per cu. metre (0·005 to ·p.m.). Thorp's method (*Anal. Chem.*, 1940, 209), in which buffered KI soln. is used for rbing $O_3$, is adapted for this purpose. The KI (2 *N*) is light-sensitive, and should be made very pure water. The streaming velocity of air is conveniently 1 litre per min. The deteration of 0·1 p.p.m. of $O_3$ then takes 2·5 hr. and curate to within ±10%. Blanks must be run $O_3$-free air.

J. P. Stern

89. **Determination of nitrogen dioxide and c oxide in air.** W. E. Gill (Gen. Electric Co., ford Atomic Products Operation, Richland, h.). *U.S. Atomic Energy Comm.*, Rep. HW-1 (Rev.), 1958, 23 pp.—Several methods of $NO_2$ pling and analysis were investigated. A simple nod was developed for the prep. of known concn. $NO_2$ and NO. In 50-ml syringes containing -absorbing reagents of the Griess - Ilosvay , colour development occurred rapidly for ur. For greatest accuracy, colour development ld be allowed to continue for 1 hr. before readsare taken. Griess - Ilosvay type reagents were pecific for $NO_2$ in that they reacted significantly NO. The phenoldisulphonic acid method for letermination of $NO_2$ gave good recoveries in n. as low as 16 p.p.m., when a 500-ml air sample used. Approx. 40% of the $NO_2$, in mixtures of and NO, was selectively adsorbed on 4 g of 0 20-mesh silica gel when the $NO_2$ concn. did xceed 100 p.p.m.

Nucl. Sci. Abstr.

3790. **Determination of particulate lead content in air. Results of tests in city traffic.** B. J. Tufts (Cloud Physics Lab., Dept. of Meteorol., Univ. of Chicago, Ill., U.S.A.). *Anal. Chem.*, 1959, **31** (2), 238–241.—Airborne particles containing Pb may be detected and the size and number of particles may be determined after reaction with a satd. soln. of tetrahydroxyquinone in 50% aq. ethanol. The reagent forms a red ppt. with Pb. The air sample is drawn through a membrane filter. The membrane is then placed on a piece of blotting paper soaked in the reagent soln. Soluble lead compounds react immediately. For the detection of insol. lead compounds, the membrane is exposed to HF vapour for 1 hr., then to $NH_3$ fumes for 3 min., and is then brought into contact with the reagent soln. on blotting paper. After the reaction is complete the membrane is transferred to a glass slide and dried. It is then mounted with a drop of immersion oil and examined microscopically. The red spots of the lead ppt. can be counted and the lead content estimated. A definite relationship exists between the original particle size and the reaction site size. The method has been used to study the emission of Pb-containing particles from automobile exhausts. Calcium ions, $Ag^+$, $Fe^{2+}$ and $Fe^{3+}$ give no reaction, while $Ba^{2+}$ give a greenish-yellow coloration.

F. L. Selfe

3791. **Determination of quinquevalent, tervalent and organic phosphorus in the atmosphere and in aqueous solutions.** R. May (Occupational Health Branch, Div. of Health and Safety, T.V.A., Wilson Dam, Ala., U.S.A.). *Anal. Chem.*, 1959, **31** (2), 308–310.—The usual colorimetric methods for the determination require P to be in the orthophosphate form. Selective oxidation procedures are described for the determination of $P^{III}$, $P^{V}$ and organic phosphorus when present together in aq. soln. Three aliquots of the sample soln. are treated as follows—(*i*) $P^{V}$ is measured with no oxidising treatment; (*ii*) $P^{V}$ is measured after oxidation of $P^{III}$ with $(NH_4)_2S_2O_8$ in HCl soln. (0·1 *N* to 1·0 *N*); (*iii*) $P^{V}$ is measured after oxidation of $P^{III}$ and organic phosphorus with $(NH_4)_2S_2O_8$ in alkaline soln. (2% NaOH). In each case the measurement of $P^{V}$ is made colorimetrically by either the molybdenum blue or the molybdovanadophosphate method. A method for atmospheric sampling is given and results are quoted.

F. L. Selfe

3792. **Determination of chlordane in air of habitations treated for insect control.** M. A. Malina, J. M. Kearny and P. B. Polen (Velsicol Chem. Corp., Chicago, Ill., U.S.A.). *J. Agric. Food Chem.*, 1959, **7** (1), 30–33.—Chlordane is determined by drawing 1000 litres of air (5 litres per min.) through two traps each containing 30 ml of *n*-butanol. The combined butanol soln. are mixed by swirling with *n*-pentane (100 ml) and the alcohol is removed by washing with water (7 or 8 × 200 ml). The pentane is dried with anhyd. $Na_2SO_4$ (5 to 10 g), and evaporated to 10 ml. This soln. is then chromatographed on a Florisil column, and the chlordane is eluted with pentane (200 ml) and determined colorimetrically with alkaline methanolic diethanolamine by a modification of Davidow's method (*J. Ass. Off. Agric. Chem.*, 1950, **33**, 886). The recovery averages 80% and concn. lower than 0·005 p.p.m. can be determined.

M. D. Anderson

3793. **Improvements relating to the testing of water for free and combined chlorine [by means of an indicator].** A. T. Palin. Brit. Pat. 813,493; date

appl. 28.11.56.—A dialkyl derivative of *p*-phenylenediamine or a salt thereof, *e.g.*, the oxalate, sulphate or hydrochloride of dimethyl- or diethyl-*p*-phenylenediamine, is used as an indicator in conjunction with a sequestering agent, *e.g.*, sodium hexametaphosphate or EDTA or its disodium salt.

J. M. Jacobs

3794. **Rapid determination of sulphate, chloride and nitrate ion in water in a single sample.** D. Ceauşescu (Inst. for Hygiene, Timişoara, Romania). *Z. anal. Chem.*, 1959, **165** (6), 424–428.—The sample is passed through a cation-exchange resin (H form) and the eluate is analysed volumetrically. The total acid is titrated with NaOH soln., with alizarin red S (C.I. Mordant Red 3) as indicator; the $H_2SO_4$ is measured by titration with $Ba(ClO_4)_2$ and the HCl with $Hg(NO_3)_2$ soln. The $HNO_3$ content is calculated from the differences. The error is generally $<1\%$.

G. P. Cook

3795. **[Determination of] silica in water. V. Salt effect on the colorimetric determination of silica in concentrated salt solution.** Iwaji Iwasaki and Toshikazu Tarutani (Anal Chem. and Geochem. Lab., Instit. of Technol., Meguro-ku, Tokyo). *Bull. Chem. Soc. Japan*, 1959, **32** (1), 32–36 (in English).—The wavelength, the kind of salt and the concn. of salts affect the salt effect in both the molybdosilicate and molybdenum blue methods, the salt effect in the former method being greater at a longer wavelength. The effect of sulphate is greater than that of chloride. The absorbance of both the molybdosilicate and the molybdenum blue complex in a salt soln. obeys Beer's law at a given wavelength when the concn. of salt and reagents remain constant. In salt soln. containing definite amounts of silica, the absorbance decreases linearly with salt concn. under these conditions. To obtain the true silica content in concentrated salt soln. by the colorimetric method, one of the following procedures should be used. (*i*) A sample soln. is diluted with $H_2O$ sufficiently for the salt effect to be neglected and the absorbance is then measured; (*ii*) a calibration curve is prepared with standard sodium silicate soln. containing the same concn. of salts as in the sample soln.; (*iii*) a calibration curve is prepared by means of standard sodium silicate soln. without added salts. This is used to determine the concn. of silica in the sample soln. (*A*) and in the sample soln. diluted with an equal vol. of water (*B*). The true silica content (*S*) is then given by $S = A + 2(2B - A)$.

I. Jones

3796. **Methods for measuring grease in sewage.** W. W. Ullmann and W. W. Sanderson (New York State Dept. of Health, Albany). *Sewage Ind. Wastes*, 1959, **31** (1), 8–19.—A chromatographic adsorption method developed for the differentiation in sewage between grease of petroleum and non-petroleum origin is described. Experimental data show that light petroleum and *n*-hexane are equally suitable as solvents, and that the precision and accuracy of the method are independent of the amount of oil present in the samples.

O. M. Whitton

3797. **Determination of oil in refinery effluents by u.v. spectrophotometry.** O. Harva and A. Somersalo (Lab. of Neste Oy Refinery, Naantali, Finland). *Suomen Kem. B*, 1958, **31** (12), 384–387.—A sample of the refinery effluent is shaken with $CCl_4$ and diluted with $CCl_4$ so as to contain 10 to 100 mg per litre of waste oil. The u.v. absorption of this soln. is measured at the maximum of 260 m$\mu$ and th concn. of the oil in the sample is calculated by mea of a standard oil soln. It is stated that this metho gives the same precision as the usual i.r. or pycn metric methods, whereas gravimetric methods giv low values.

E. Sjöström

3798. **Behaviour and determination of radium-I radium-D and thorium-B in natural waters.** C Alberti, C. Bettinali and F. Salvetti (Chem. Lab Geomineral. Div., C.N.R.N., Inst. Gen. and Inor Chem., Univ. of Rome). *Ann. Chim., Roma*, 195 **49** (1), 193–198.—Radioactive lead isotopes i samples of water are extracted as the dithizonat and the rate of decay in $\beta$-activity is compare with that of standard soln. of Ra-B, Th-B an Ra-D. The half-lives of these 3 isotopes diff considerably, and hence the concn. of the individu isotopes may be determined. By the metho described it is also possible to determine the conten of Rn and of the Ra and ThX ultimately produce

A. G. Cooper

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*See also Abstract*—**3648**, Determination of Ca i water.

## Agricultural analysis

*Soil, fertilisers, herbicides, pesticides, animal feeding-stuffs.*

3799. **Determination of boron in treated woo** W. J. Wilson (Forest Res. Inst., Whakarewarew Rotorua, N. Zealand). *Anal. Chim. Acta*, 1958, 1 (6), 516–519.—Two modified procedures are d scribed, one for rough sorting of impregnated timb and one for more precise determinations. F rough sorting, a cross-section is sprayed wit turmeric extract (10% in ethanol), allowed to dr and then sprayed with an acid soln. (20 ml of con HCl in 80 ml of ethanol saturated with salicyl acid). With *Pinus* species, the second soln. modified (10 ml of HCl, 90 ml of ethanol and 10 of salicylic acid). After drying, the wood show distinct gradations of colour corresponding to th boric acid content (bright red $\equiv 0{\cdot}3\%$, brown - re $\equiv 0{\cdot}25\%$, yellow - brown $\equiv 0{\cdot}25\%$, yellow $0{\cdot}1\%$). Samples showing $<0{\cdot}25\%$ are analyse chemically. For precise determinations the standa ashing technique is modified by adding to 5 g powdered wood 10 ml of $Ba(OH)_2$ soln. (7·5% 1% v/v $HNO_3$) and drying before ignition.

T. R. Andrew

3800. **Determination of urea in agricultural nitr gen solutions.** D. K. Gullstrom and P. A. Der kovich (Res. Dept., Standard Oil Co., Whitin Indiana). *J. Agric. Food Chem.*, 1959, **7** (1), 26–2 —Urea is determined in the presence of $NH_3$ and/ $NH_4NO_3$ by decomposing with $HNO_2$, absorbing t $CO_2$ evolved in a soln. of $Ba(OH)_2$ and $BaCl_2$, a titrating the excess of base. Dissolved $CO_2$ is fi removed from the soln. by adding $H_2SO_4$ and bu bling with N, before adding $NaNO_2$. The meth has proved simple and rapid in routine use, and repeatable to $\pm 2{\cdot}0\%$ of the urea present.

M. D. Anderson

3801. **Colorimetric determination of phospho acid in fertilisers by the molybdovanadophosph method. II. Effect of ingredients and maski** Mitsunari Matsubara (Sumitomo Chem. In Niihama, Ehime-ken). *Japan Analyst*, 1958,

571–578.—The effect of various ingredients in erphosphate fertilisers was examined by the use he reagent reported in Part I (*cf. Anal. Abstr.*, 9, **6**, 2381). The effect of silicic acid decreases n increase in $HNO_3$ concn., but the colour fades er in $HNO_3 > N$. In the absence of citric acid, following composition appears to be the best— $_4VO_3$ 1·12 g, $(NH_4)_2Mo_7O_{24}.4H_2O$ 27·0 g, and $O_3$ (sp. gr. 1·38 to 1·40) 250 ml per litre (20 ml $<8$ mg of $P_2O_5$ per 100 ml of the final soln.). the presence of citric acid (0·34 g), the amount molybdate is increased to 50 g and the final cn. of $HNO_3$ is adjusted to 0·7 *N*. K. Saito

802. **Chemical method for estimation of niacin [nicotinic acid] in poultry feeds and premixes.** S. Mohan, B. L. Reid and J. R. Couch (Dept. of ultry Sci. and Biochem. and Nutrition, Texas & M System, College Station, U.S.A.). *J. Agric. od Chem.*, 1959, **7** (1), 42–44.—Nicotinic acid is ermined in feeding-stuffs by autoclaving with $H_2SO_4$, filtering, decolorising the filtrate with manganate if necessary, neutralising to pH 6·5 6·8, and treating with cyanogen bromide to oduce a colour which is measured at 420 mμ. coveries of added nicotinic acid averaged 98·6%, d results agreed well with those by microbiological ay. M. D. Anderson

3803. **Chromatography of organic insecticides. Separation on paper treated with 2-phenoxyanol [phenylCellosolve].** Takashi Shishido and sana Suwanai (Nat. Inst. of Agric. Sci., Nishiara, Kita-ku, Tokyo). *J. Agric. Chem. Soc. pan*, 1958, **32** (12), 956–960.—By the use of a xture of 2-phenoxyethanol and acetone (5 : 1, vol.) as stationary phase, and a mixture of *n*-xane, $CHCl_3$, benzene and methyl cyanide as veloper, 25 organic insecticides, including various ganophosphorus and chlorine compounds, were amined and the $R_F$ values determined. For loro compounds, *n*-hexane saturated with methyl anide was the best developer and for phosphorus mpounds a mixture of *n*-hexane, $CHCl_3$ and benne (*e.g.*, 10 : 2 : 1) was suitable. The separation Isochlorthion, parathion-ethyl and O-ethyl *p*-nitrophenyl phenylphosphorothionate was not hieved. K. Saito

3804. **Application of Janovsky's and Mohler's actions to the detection of benzene hexachloride exachloro*cyclo*hexane].** E. Rathenasinkam (Gov. nalyst's Lab., Colombo, Ceylon). *Analyst*, 1958, , 688–689.—In the test based on Janovsky's action, 0·5 to 1 ml of nitration acid (5 g of $KNO_3$ 100 ml of $H_2SO_4$) is placed in a Cavett flask *nalyst*, 1954, **79**, 125) and 0·2 ml of a soln. of xachloro*cyclo*hexane (**I**) in glacial acetic acid, with ree fragments of magnesium wire, is added to e stopper-cup and the stopper is immediately serted. After 30 min. the cooled nitration acid is uted with water (20 ml) and extracted with ethyl ether. The extract is washed with 2% aOH soln. and saturated NaCl soln. and is filtered rough cotton wool and $Na_2SO_4$ into a test-tube. quid paraffin (4 drops) is added to the filtrate, the ner is removed by evaporation, the residue is ssolved in 1 ml of a mixture of acetone and abs. nanol (1 : 1), 0·1 ml of a 4% soln. of KOH in ethanol is added and the tube is stoppered. A mson colour develops in 2 min. The test is nsitive to 5 μg of **I**. In the test based on Mohler's action, the dechlorination and nitration are rried out as described above, but with only 0·5 ml of nitration acid. After 30 min. the nitration acid is diluted with 2·5 ml of water, 5 ml of 25% aq. $NH_3$ is added and then 2 ml of 2% hydroxyammonium chloride soln., and the mixture is transferred to a stoppered tube. A violet colour develops slowly. The test is sensitive to 0·25 mg of **I**.

A. O. Jones

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*See also Abstracts*—**3527**, Determination of Co in agricultural material. **3648**, Determination of Ca in soil extracts. **3814**, Soil-perfusion apparatus.

## 5.—GENERAL TECHNIQUE AND APPARATUS

### General

3805. **Precision of some procedures in pharmaceutical analysis. I. Use of a pipette and a burette.** A. R. Rogers (Sch. of Pharm., Brighton Tech. Coll., England). *J. Pharm. Pharmacol.*, 1958, **10**, Supplement, 98T–105T.—Estimates have been made of the variance associated with the calibration of a number of 10- and 20-ml pipettes and 50-ml burettes of Grade-B quality, and of the variance associated with their use by students. Comparison with the variance of the results of students performing simple titrations with this apparatus indicates that the chief components of the latter variance have been identified. A. R. Rogers

3806. **New method for the measurement of the density of liquids.** J. Krutzsch (Villacher Strasse 52, Munich, Germany). *Chimia*, 1958, **12** (11), 324–325.—An apparatus utilising the comparison of heights of liquid columns in determining $\rho$ is described (*cf. Klin. Wochschr.*, 1943, **22**, 469). A capillary tube dips into the test liquid and its open top communicates with a U-tube with one short limb. Both tubes are connected to a syringe acting as a piston pump. The U-tube contains a non-volatile oil of known $\rho$. When the syringe piston is retracted, the liquids rise in their respective tubes. The bulk of the test liquid is then lowered manually so that contact between its surface and the liquid column is broken. The test liquid is allowed to rise until the head of the column is in a horizontal part of the capillary. The apparatus is then isolated from the syringe by closing a screw-clip and the lengths of the liquid columns are measured. Viscosity and surface tension have no effect, and temperature changes have little effect on the determinations, which require 3 ml of liquid, occupy 2 min., and are accurate to three decimal places. The method is used for pharmaceutical and clinical fluids and extracts. J. P. Stern

3807. **Automatic reader for precision balances.** L. R. Macurdy and H. A. Bowman (Nat. Bur. of Standards, U.S.A.). *Instrum. and Automation*, 1958, **31** (12), 1972–1974.—A photo-electric beam-position recorder automatically indicates beam-position and turning points with a precision of 0·0001 in., giving an approx. 40-fold increase in readability sensitivity. G. Skirrow

3808. **New absorption pipette and magnetic shaker for the constant-volume gas-analysis apparatus.** P. R. Chapman and P. A. Murche (N. Thames Gas Board, Fulham, London). *Chem. & Ind.*, 1958, (46), 1504–1505.—Diagrams of the pipette and shaker are given. The top of a plunger containing a soft iron core and weighted with mercury floats on

the mercury surface in the pipette. The plunger is caused to oscillate 100 times per min. by a make-and-break current through a 9-ohm, 12-V a.c. solenoid. A double cam fitted to a 12-V, 50 r.p.m. motor depresses a spring-loaded bar resting against the control button of a micro-switch in the solenoid circuit; the current to solenoid and motor is controlled by a timer switch. Reagents in reservoirs are connected to the pipette through a manifold and are protected by a layer of paraffin oil; furnaces are electrically heated and easy regeneration of the catalyst is possible. The complete analysis time for fuel gas is 75 min. P. D. PARR-RICHARD

3809. **Automatic apparatus for elementary organic analysis.** F. Vojtěch (Res. Inst. Org. Synth., Pardubice-Rybitví, Czechoslovakia). *Chem. Průmysl*, 1958, **8** (12), 633–636.—Three types of automatic apparatus for organic analysis and their use are described. (*i*) A simple apparatus for the determination of N based on the Dumas - Zimmerman principle (*Mikrochemie*, 1943, **31**, 42), in which the combustion is carried out with successive switching of the heating circuits; (*ii*) apparatus for the determination of C and H according to Pregl's procedure, suitable also for rapid catalytic combustion (Synek and Večeřa, *Chem. Listy*, 1955, **49**, 1891) on the semi-micro- and micro-scale (Körbl, *Chem. Listy*, 1955, **48**, 858); (*iii*) universal apparatus for the determination of C,H,N,S and halides on the semi-micro- and micro-scale; two samples can be analysed simultaneously. Descriptions and illustrations of the apparatus together with manipulative details are given. J. ZÝKA

3810. **Mineralisation apparatus for the determination of nitrogen by the Kjeldahl and phosphorus by the Belcher and Godbert methods.** X. Bilger and G. Mangeney. *Bull. Soc. Chim. France*, 1958, (11–12), 1539–1540.—An apparatus is described in which fumes from a Pyrex-glass mineralisation tube with a side-arm are removed through a small glass manifold into a vacuum filtration flask. The tube is loosely stoppered with a flattened glass ball through which passes a Gernez tube made by forming a bulb on the end of a 4-mm tube and drawing in a concavity of 1 to 2 mm. E. J. H. BIRCH

3811. **Apparatus for the controlled flame combustion of filter-paper.** M. Homma and A. E. Greendale (Naval Radiological Defense Lab., San Francisco). *U.S. Atomic Energy Comm.*, Rep. USNRDL-TR-285, 1958, 16 pp.—A new apparatus and technique are described for the controlled flame combustion of filter-paper and cloth. The sample is burned in an atmosphere of oxygen at a reduced pressure within a Pyrex-glass cylinder. A detailed description is given of the operation of the apparatus. The many advantages of this system over previous methods are enumerated. The apparatus can be scaled up or down in size and can also be used with gases other than oxygen. Since it is possible to contain the sample completely during the combustion and to collect the products of combustion, it appears to be an extremely efficient system for quant. determinations and for use with radioactive materials and toxic chemicals.

NUCL. SCI. ABSTR.

3812 **Improvements in or relating to devices for determining the oxidising or reducing characteristics of an atmosphere.** Robertshaw-Fulton Controls Co. [Inventor: C. D. Lawhon]. Brit. Pat. 812,607; date appl. 4.5.56. U.S.A., date appl. 8.8.55.—The device comprises a pair of thermocouples one of which has a housing (*e.g.*, of copper oxide) thermally affected by a reducing atmosphere, while the other has a housing (*e.g.*, of carbon) which is thermally affected by an oxidising atmosphere. The thermocouples, which are inserted in suitable apertures in the wall of the chamber, are connected so that their e.m.f. are opposed. J. M. JACOBS

3813. **Quantitative sedimentation analysis with a sedimentation pipette.** W. Kromrey. *Chemiker Ztg*, 1959, **83** (1), 13–16.—In the technique described the normal gravimetric analytical procedures are used for the determination of ions, but the amount of pptd. material is measured as the height of a column of solid, and not by weight. It is shown that this height (in mm) is related to the amount of ion present in soln., and that by using standard soln. a direct conversion of mm to mg is possible. The pptn. is carried out in a sedimentation pipette (described) and the ppt. is centrifuged under standard conditions of speed and time. Methods are given for the determination of 20 ions, and of picric acid, and by the use of suitable pptg. agents this list can be extended. The technique is relatively simple, and each determination requires only 2 to 5 ml of soln. It can be used for the analysis of blood, serum and urine. D. B. PALMER

3814. **Modified design of the Audus soil-perfusion apparatus.** C. M. Sims and F. M. Collins (Dept. of Bacteriol., Univ. of Adelaide, S. Australia). *Analyst*, 1958, **83**, 699–701.—In the apparatus described by Lees and Quastel (*Biochem. J.*, 1946, **40**, 803), soil was continuously perfused with dil. $(NH_4)_2SO_4$ soln., the rate of nitrification of the $NH_3$ being followed by determination of $NO_3^-$ in the perfusate. The modified form of this apparatus devised by Audus (*Nature*, 1946, **158**, 419), now further modified, is described. Graphs of results obtained with the modified apparatus resemble those reported by Lees and Quastel (*loc. cit.*), the only difference in the performance of the modified apparatus being the transient accumulation of nitrite-N in the perfusate before $NO_3^-$ are detected. The apparatus is in one piece and among its other advantages are its smallness, its independence of external support, and the possibility of accommodating more than 20 units operated by a single water-pump through a manifold fitted in an incubator 4 ft. × 3 ft. × 2 ft. A. O. JONES

3815. **Improvements in or relating to viscometers.** "Shell" Research, Ltd. [Inventor: J. F. Hills]. Brit. Pat. 813,735; date appl. 2.8.57.—A bob is mounted in a fixed cup so that it is free to rotate about a spindle to which a second cup is rigidly attached and hence also rotates about the same axis. A second bob is mounted in the second cup and is coupled to an electric motor so that it rotates about a second spindle. In operation, one of the cups is filled with liquid of known viscosity and the other with the sample of which the viscosity is required. The latter is determined from the viscosity of the first liquid and the relative rates of rotation of the bobs. J. M. JACOBS

## Chromatography, ion exchange, electrophoresis

3816. **General method for detection and recording of component bands in chromatography with liquid eluents.** J. C. Sternberg and L. M. Carson (Michigan State Univ., E. Lansing, U.S.A.). *J. Chromatography*, 1959, **2** (1), 53–57.—A detector for use with

string or column chromatography is ɔed. Two wicks are situated in a temp.-ɔlled cell filled with the satd. vapour of the g solvent. One wick is continuously satd. he eluent and the other with the eluate from ɔlumn. The arrival of a dissolved component a change in the v.p. of the eluent and hence e evaporative heat-loss of that wick. The difference between the wicks is measured by istors connected to a bridge circuit and ler. The method is of wide application.

G. BURGER

7. **Apparatus for the quantitative introduction quid samples into chromatographic columns.** ngliar and J. Brida (Res. Inst. of Acetylene ., Nováky, Czechoslovakia). *Chem. Průmysl*, **8** (11), 588–589.—The apparatus described is constructed. The sample is sealed into a ampoule, and placed in an easily destructible holder inserted in the chromatographic ın immediately before the filling. A small iron is moved electromagnetically to break the ɔule, the sample is evaporated and transferred he column by the carrier gas. The apparatus table for the handling of 5 to 20 mg of com-ds having b.p. from −15° upwards.

J. ZÝKA

18. **Fraction-collector modifications.** E. A. y (E. Reg. Res. Lab., Agric. Res. Service, Dept. of Agric., Philadelphia, U.S.A.). *Anal.*, 1959, **31** (2), 317–318.—The two modifica-described are used in the ion-exchange chrom-raphy of amino acids. A capillary inflow arm bstituted for the wider tube frequently used drop-counting fraction collectors; this mini-s the uptake of impurities from the laboratory nd improves the uniformity of dropping of the e. An auxiliary counter is used to switch the rol contacts of the relay of the heating bath, h controls the temp. of the columns, from one nostat to another at any given fraction number.

A. R. ROGERS

19. **New paper-chromatographic procedure.** H. ɔensteiner (Fed. Inst. for Testing Veg. Products, enheim/Rhg, Germany). *J. Chromatography*, , **2** (1), 113–114 (in German).—A procedure for ɔontal chromatography is described in which the matogram can be extended by moving the and the paper.

G. BURGER

20. **Circular paper chromatography.** A. Miss F. Segal (Chem. Res. Inst., Min. for Petroleum Chem. Ind., Bucharest, Romania). *Z. anal.*, 1959, **165** (1), 1–5.—The advantages of lar over ascending or descending paper chrom-raphy are discussed, and an improved and lified technique is described in which the paper ld horizontally between two Petri dishes and with solvent by means of a thread of mercerised n, artificial silk, wool, or other material. thread dips into the solvent and passes through e at the centre of the paper where the material e developed is placed. The rate of solvent port can be controlled by choice of the material ength of the thread. Reproducibility is very and the method has been satisfactorily used he separation of amino acids, higher fatty , sugars, etc.

J. P. STERN

21. **Semi-automatic multi-pipetting device for chromatography.** J. W. Porteous (Marischal Univ., Aberdeen, Gt. Britain). *J. Chromato-y*, 1959, **2** (1), 58–64.—The apparatus described comprises a paper holder and a pipette holder. Large vol. of soln. can be applied in 2 to 5-$\mu$l portions to 12 papers simultaneously. Provision is made for drying each portion before the next addition. Constructional details are given.

G. BURGER

3822. **Simple ascending paper-strip chromatography device for rapid exploratory studies.** G. J. Miller and R. J. McColloch (Dept. of Agric. Res. Chem., Univ. of Wyoming, Laramie, U.S.A.). *Anal. Chem.*, 1959, **31** (2), 320–321.—A glass tube (1 in. diam.) is used as the chromatography chamber and the paper strip is suspended from a thermometer-suspension stopper and held taut by a glass weight hung from the bottom of the paper strip.

A. R. ROGERS

3823. **Appearance of artefacts on chromatograms of quaternary ammonium compounds.** C. Crocker (Inst. of Biophys., Univ. of Brazil, Rio de Janeiro). *J. Chromatography*, 1959, **2** (1), 115–116.—Residual traces of trichloroacetic acid in concn. as low as 0·2% can produce artefacts in chromatograms of quaternary ammonium compounds run with alkaline solvents. They have been observed with choline and several synthetic curares. Similar artefacts have been observed by other authors in chromatograms of adrenaline, histamine and thyroxine run with acid solvents.

G. BURGER

3824. **Review of gas - liquid chromatography.** C. J. Hardy and F. H. Pollard (Univ., Bristol, England). *J. Chromatography*, 1959, **2** (1), 1–43.—The published work on the theoretical principles, apparatus, techniques and applications of gas - liquid chromatography is critically reviewed, with 619 references.

G. BURGER

3825. **New apparatus for gas-chromatographic analysis.** W. Virus (Dr. Virus KG, Bonn, Rheinweg 159). *Erdöl u. Kohle*, 1958, **11** (12), 867–868.—The "Gasofract" gas chromatograph is described. A 16-metre column, built from sections, is housed, together with the thermal-conductivity cell, pre-heater and inlet system, in a thermostat capable of maintaining the temp. constant to $\pm$0·1°. The working range is 40° to 250°. All the column controls and the bridge circuit are contained in the column unit. The sample may be liquid or gaseous. A separate recording unit records and integrates the chromatogram, so that peak areas are shown directly. Seven sensitivity ranges are available on a chart width of 25 cm. Suitable stationary phases are recommended for several separations.

G. BURGER

3826. **Analysis of gases.** Esso Research and Engineering Co. Brit. Pat. 811,744, date appl. 1.8.56. U.S.A., date appl. 1.8.55. (Addition to Brit. Pat. 762,008, dated 2.2.54.)—The method of analysis claimed in Brit. Pat. 762,008 is improved by separating the gaseous mixture into various fractions by means of chromatography and using the fractions from the chromatographic separation as the first mixture of gases in the method described in Brit. Pat. 762,008.

J. M. JACOBS

3827. **Improvements in and relating to gas analysing apparatus.** Cambridge Instrument Co., Ltd. [Inventors: G. Jessop and H. V. Beck]. Brit. Pat. 812,714, date appl. 25.6.56.—In apparatus embodying a katharometer or other means involving the utilisation of temp. changes of electrically heated

thermal elements, these elements are supplied from a mains unit comprising a transformer having a low leakage inductance (*e.g.*, 100 $\mu$H) and a secondary winding having, or connected in series with, a resistance of $\lt 1$ ohm. J. M. Jacobs

3828. **Process for the continuous separation of gas mixtures by means of gas chromatography.** Deutsche Erdol-A.-G. Brit. Pat. 810,767, date appl. 13.11.57. Germany, date appl. 17.11.56.—The gas mixture to be separated, which comprises slow- and fast-moving components or groups of components and a carrier gas, is passed continuously through a separation column containing a solid phase moving in countercurrent to the direction of flow of the gas mixture, and at a velocity intermediate between the velocity of the slowest- and that of the fastest-moving components. J. M. Jacobs

3829. **Continuous gas chromatography. Procedure for continuous two-phase countercurrent separation of a multicomponent mixture applying temperature gradients.** W. Kuhn, A. Narten and M. Thurkauf (Phys.-Chem. Inst., Univ., Basel). *Helv. Chim. Acta*, 1958, **41** (7), 2135–2148.—Separation of several components may be effected by running two mobile phases in countercurrent and maintaining a temp. gradient along the column. As the distribution coeff. vary with temp., various components collect at different places along the column and may be removed.
M. H. Sawistowska

3830. **Characterisation of organic compounds by gas chromatography. I. Retention indices of aliphatic halogen compounds, alcohols, aldehydes and ketones.** E. Kováts (Org.-chem. Lab., Tech. Hochschule, Zürich). *Helv. Chim. Acta*, 1958, **41** (7), 1915–1932.—The retention index, a value related to the vol. of the gas constituting the stationary phase at the maximum concn. of the chromatographed substance, is characteristic for different substances and provides means of identification. Data for a number of compounds are tabulated. For the separation of two compounds there must exist a certain minimum difference in the values of their retention indices.
M. H. Sawistowska

3831. **Gas chromatography of polar compounds using a non-polar liquid phase.** E. C. Ormerod and R. P. W. Scott (Benzole Producers Ltd., Watford, Herts., England). *J. Chromatography*, 1959, **2** (1), 65–68.—Poor separation in the gas chromatography of polar materials with a non-polar stationary phase is due to adsorption on the support. Separation is greatly improved by coating brick dust with an equal weight of silver by the Rochelle salt method. The ground brick is degreased, treated with the silvering soln. and de-gassed under reduced pressure before the reducing soln. is added. Deposition of gold on brick was patchy and unsatisfactory. Coatings of gold on silvered brick or of nickel from $Ni(CO)_4$ are suggested as possible improvements.
G. Burger

3832. **Micro-sample introduction system for gas chromatography.** R. L. Bowman and A. Karmen (Nat. Heart Inst., Bethesda, Md., U.S.A.). *Nature*, 1958, **182**, 1233–1234.—The apparatus described enables small vol. of samples in the microgram range to be directly introduced into the system. Samples are sealed in small glass capillaries in which the vol. can be accurately measured; capillary is crushed in the gas stream at column inlet. H. F. W. Kirkpatrick

3833. **Collection unit for gas - liquid chromatography under reduced pressure.** B. M. Craig, T. Mallard and L. L. Hoffman (Prairie Reg. Lab., N Res. Council, Saskatoon, Saskatchewan, Canad *Anal. Chem.*, 1959, **31** (2), 319–320.—In the u described, each component emerging from a g chromatographic column can be collected separat without disturbing the pressure in the syste The unit is also suitable for operation at atm pheric pressure. K. A. Proctor

3834. **Response time and flow sensitivity detectors for gas chromatography.** L. J. Schmau [Res. Dept., Standard Oil Co. (Indiana), Whiti Ind., U.S.A.]. *Anal. Chem.*, 1959, **31** (2), 225–230 A quantitative relationship exists between ba shape and the ratio of response time to band wi in gas chromatography. To prevent band broad ing and asymmetry, the response time of t detector must be small. K. A. Proctor

3835. **Apparatus for automatic colouring a decolorisation of electrophoresis papers.** O. P. F and B. Andersen (Central Lab., Ullevål Hos Oslo, Norway). *Scand. J. Clin. Lab. Invest.*, 19 **10** (3), 344.—The papers are carried on a plas framework which is rotated in a semi-cylindri ceramic trough by an electric motor. A plas hood covers the trough and frame. The trou contains the staining or decolorising soln., into whi the papers dip. Rotation times depend on t staining technique employed; with a satd. soln. Amido-black 10B (C.I. Acid Black 1) in methanol rotation time of 20 min. is usually sufficient.
D. W. Moss

## Optical

3836. **Transmission characteristics of some inte ference filters for use in flame photometers.** R. Bond and H. C. T. Stace (C.S.I.R.O., Div. of Soi Adelaide, S. Australia). *Analyst*, 1958, **83**, 67 683.—The transmission characteristics of sev combination interference-absorption filters and o gelatin absorption filter for the isolation of t sodium D line have been determined. The tra mission characteristics were determined spectr photometrically and the filters were then examin in a flame photometer to measure the interferen caused by radiations emitted by other elemen during the determination of Na in soil extracts a minerals. To determine the magnitude of the expected interferences, soln. containing 20 mil equiv. per litre of salts of Li, K, Rb, Cs and were examined in the flame photometer and th apparent Na content determined with each filt One filter indicated no apparent Na content af correction for Na present as impurity except w the soln. of $CaCl_2$. With the other filters the app ent Na found (corrected) ranged from 0·003 0·132 milli-equiv. per litre. The component err contributing to the total error are discussed.
A. O. Jones

3837. **High-sensitivity, recording, scanning fla spectrophotometer.** M. T. Kelley, D. J. Fisher a H. C. Jones (Nat. Lab., Union Carbide Nuclear C Oak Ridge, Tenn., U.S.A.). *Anal. Chem.*, 1959, (2), 178–183.—The instrument described posses

advantages of increased precision and dependty (arising from the use of a chart recorder), ction of hazards in radioactive analyses, and reduction of flame, background, anion and salt ferences. Generally, the relative standard ation for analyses is $<1\%$ and linear calibra- curves are obtained over reasonable concn. es. Considerations governing the choice of ous components such as the recorder, monomator and photomultipliers are discussed.
K. A. Proctor

38. **Three new spectrophotometers.** E. Lüscher rohm A.-G., Herisau, Switzerland). *Appl. troscopy*, 1958, **12** (6), 172–174.—Three comcial instruments are described—an interference colorimeter (400 to 700 m$\mu$), a prism spectrometer (300 to 750 m$\mu$) and a silica prism - prism - grating spectrophotometer (210 m$\mu$ to
K. A. Proctor

39. **Local spectral analysis.** A. G. Komarovskiĭ. *t. Nauch.-Issled. Tekhnol. i Mashin.*, 1957, **84**, 198.—A universal generator, producing, in tion to the usual spark and arc discharges, a -frequency discharge, a strong spark pulse harge of low voltage, and an a.c. arc pulse harge, is described and the procedure outlined. pper wire, 8 to 9 mm in diam., shaped to a cated cone with a working surface of 1 to 1·5 mm, was found more satisfactory as an upper rode than aluminium, nickel, iron or carbon. high-frequency discharge was suitable for the tral analysis of surface layers along the edges ot-cracks in welds of high-alloyed steel. The aces of these cracks were of a different composi- than the metal of the weld and had to be oved by grinding. The most suitable spectral pairs for the determination of Mo, Ni, Si, Mn, W, Ti, V, Co, Al and Nb were determined and lated. The low-voltage spark pulse discharge, ng $10^{-2}$ to $10^{-5}$ sec., one impulse of which was factory for an analysis, gave additional lines h were absent in other light sources; the lines ir were also absent so that it could be used for determination of H, N and O in steel. To lise the surface of analysis, prevent flame migra-, and intensify the lines, the spark contact was e through a hole 0·1, 0·5, 1·0 or 1·2 mm ctured through a layer of insulating plastic or lac 1 or 0·2 to 0·6 mm thick. Chem. Abstr.

40. **Constant-current arc source for spectronical analysis.** L. E. Owen (Tech. Div., Good- Atomic Corp., Portsmouth, Ohio, U.S.A.). *l. Spectroscopy*, 1958, **12** (6), 178.—The source ribed operates from a single-phase power supply, ides various controlled current outputs at rent levels, incorporates ignitor and timing its and provides for optional earthing of the tive or positive line. K. A. Proctor

41. **Effect of spectrum carbons on spectrohic analysis.** H. H. Rüssmann (Ringsdorffke G.m.b.H., Bad Godesberg-Mehlem, DBR). *Chim. Acad. Sci. Hung.*, 1959, **18** (1–4), 101– (in German).—The basic differences between hite and carbon electrodes are described, and effect of both types on spectrographic analysis scussed. The temp. of the d.c. arc with both rodes has been found from the intensity curve e CN bands, the carbon arc being the hotter by ox. 700° K. The phenomenon of "creeping," experienced with d.c. arcs when elements of low ionisation potential are excited, is discussed, and methods for overcoming this are suggested. The influence of the two types of electrode on the analysis of soln. has been studied, together with the effect of porosity of the electrode. H. M.

3842. **Simple device for the spectrochemical analysis of minerals in an inert atmosphere using the Stallwood jet.** D. M. Shaw, O. Wickremasinghe and C. Yip (McMaster Univ., Hamilton, Ontario, Canada). *Spectrochim. Acta*, 1958, **13** (3), 197–201.—Details are given of a partially closed chamber, made from Pyrex-glass tube, a piece 0·75 in. in diam. and 3 in. long being attached to a piece of 0·25 in. diam. by a T-joint; with this chamber, air can be completely excluded from the arc, and cyanogen bands eliminated from the spectra. By using a gas mixture of argon and oxygen (1 : 1), overall background is reduced and sensitivity is enhanced. Preliminary work on the determination of Pb, Ga, Cu, Sn and Li in silicate minerals is discussed. E. G. Cummins

3843. **Quantitative determination of solids by infra-red spectroscopy and the potassium bromide disc technique.** J. B. Jensen (Specialitetskontrollen, Copenhagen, Denmark). *Dansk Tidsskr. Farm.*, 1958, **33** (11–12), 205–220, 221–235.—The literature is reviewed and discussed. To obtain the maximum base-line extinction and satisfactory spectra, repeated grinding (usually 3 to 5 times for 1 min.) and pressing is less laborious than one grinding for the requisite time (1 hr.), and gives satisfactory results for 16 test substances. A single vibrator-grinding for 3 to 5 min. achieves the same result for 9 of the substances, but fails to do so for the others; in such cases satisfactory spectra can generally be obtained by heating the discs at 100° for 5 min. With prednisolone, which fails to give satisfactory spectra with either of the grinding techniques, the heat treatment has proved successful. (35 references.) P. S. Arup

3844. **Potassium bromide pellet technique.** A. L. Olsen (Chem. Div., U.S. Naval Ordnance Test Station, China Lake, Calif., U.S.A.). *Anal. Chem.*, 1959, **31** (2), 321–322.—A simple, evacuable and easily manipulated die, designed for use in the ARL-Dietert briquetting press and employing a new technique of pressing the $\frac{7}{8}$-in.-diameter pellet directly into a 1-in.-diameter ring, is described. The pressed disc fits directly into the Perkin-Elmer demountable cell holder or into the specimen holder of the high-temp. cell. The discs obtained show max. transmittances of 89·5% with a spread of 2 to 3% between max. and min. transmittances.
K. A. Proctor

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*See also Abstract*—**3367**, Spectrographic techniques.

## Thermal

3845. **Differential thermal analysis apparatus.** F. W. Wilburn (Pilkington Bros. Ltd., St. Helens, Lancs., England). *J. Sci. Instrum.*, 1958, **35** (11), 403–407.—The rate of heating is servo-controlled to any selected value within the range 6° to 20° per min. Curves are obtained on a chart recorder in which the pen position is determined by the potential

difference between the sample and reference materials, and the chart position is determined by the potential of the thermocouple in the reference material. Temperature differences can be detected to within 0·1°. G. SKIRROW

3846. **Automatic micro-analytical apparatus for the determination of gases in metals.** Saburo Yanagisawa, Michiharu Seki, Yoshikazu Watanabe and Shigeru Nakamura (Dept. of Appl. Chem., Fac. of Engng, Keio Univ., Tokyo, Japan). *Mikrochim. Acta*, 1959, (1), 1–8 (in English).—An apparatus is described for the automatic micro-analysis of the gases ($CO_2$, CO, H, N) evolved on vacuum fusion of steel (0·3 g). The passage of gas through the system is controlled by 13 electromagnetically operated mercury cut-offs which are programmed by micro-switches arranged on a rotating drum. The gases are collected in a const. vol. and the pressure after each treatment is recorded by means of a rotary McLeod gauge modified by the inclusion of a platinum resistance wire in its capillary, to permit electrical indication of pressure. The time required for evolution of gases from the sample is 10 min. and, for their subsequent analysis, 13 min. Results are quoted for a specimen containing 0·0043% of O and 0·0043% of N.

T. R. ANDREW

## Electrical

3847. **A polarograph with a new recording device.** J. Peizker (Polarographic Inst., Acad. Sci., Prague). *Chem. Listy*, 1958, **52** (11), 2195–2197.—The automatic compensator previously described (*Chem. Listy*, 1958, **52**, 2169) has been found suitable for the construction of a new type of pen-recording polarograph, which enables a very small reference electrode of high resistance to be used. The current between the reference electrode and the corresponding part of the polarographic circuit is completely compensated. The arrangement can be used for special cases of coulometric micro-determinations or as a potentiostatic method for use with the dropping mercury electrode when studying the products of electrode reactions under polarographic conditions. J. ZÝKA

3848. **Heyrovský circuit for derivative polarography.** Yasushi Mashiko, Noboru Hosoya and Minoru Akimoto (Hot Spring Res. Centre, Kashiwagi, Shinjuku-ku, Tokyo). *Japan Analyst*, 1958, **7** (11), 702–706.—The Heyrovský circuit for derivative polarography (*Chem. Listy*, 1946, **40**, 222) was modified so as to superpose the $\triangle E$ on the mercury anode side. By this method no pulse current due to the mercury drop appears on the derivative current *vs.* applied voltage curve, provided that the dropping mercury cathode is properly adjusted. When the effect of voltage-drop due to the *iR* term is corrected, the peak voltage of the graph coincides with the half-wave potential of a reversible system (*e.g.*, $Cd^{2+}$ in KCl) associated with a large capacitance (*e.g.* 2000 $\mu$F). K. SAITO

3849. **Influence of poly(vinylpyrrolidone) on the maxima of some polarographic curves.** L. Vignoli and B. Cristau (Lab. de Pharm. et Toxicol., Fac. de Méd. et Pharm., Marseille, France). *Chim. Anal.*, 1958, **40** (12), 458–459.—Poly(vinylpyrrolidone) (**I**) is a white powder, very soluble in water, and of mol. wt. between 30,000 and 100,000. It gives no waves in cathodic polarography. In a 0·005 *N* s of KCl satd. with air, a concn. of **I** of 20 mg litre completely suppresses the oxygen maxim and the height of the wave is not affected by 50 per litre of **I**. With 0·005 *M* Pb in 0·1 *M* KCl, maxima of Pb are little affected by concn. of **I** fr 1 to 5 mg per litre, but the height of the wav affected by concn. $\geqslant$1 mg per litre. In a soln As (50 $\mu$g per ml in 2 *N* HCl), two waves are trac the first without, the second with, maxima. amounts of **I** (>100 mg per litre) required to eff the maxima of the second wave very seriou weaken the first wave. R. E. ESSER

3850. **Drop-scale chronopotentiometry.** R. Iwamoto, R. N. Adams and H. Lott (Dept. Chem., Univ. of Kansas, Lawrence, U.S.A *Anal. Chim. Acta*, 1959, **20** (1), 84–88.—Appara for chronopotentiometry is described in wh both mercury and platinum working electrodes used. The method is illustrated by the analysis single drops of soln. containing $I^-$, $Fe(CN)_6$ $Fe(CN)_6^{3-}$ and $Zn^{2+}$. The analysis time is 1 t min. and a detectable signal can be obtained fr a drop containing $3{\cdot}5 \times 10^{-10}$ equiv. of $I^-$. W. T. CARTE

3851. **Mercury chloride film anode. I. Study the characteristics of a mercury chloride film an by chronopotentiometric methods.** T. Kuwana a R. N. Adams (Dept. of Chem., Univ. of Kans Lawrence, U.S.A.). *Anal. Chim. Acta*, 1959, (1), 51–60.—In $Cl^-$ concn. of 0·2 to 0·3 *M* and us c.d. of 100 to 400 micro-amp. per sq. cm, the m cury chloride film anode can be used for the oxi tion of several organic compounds. Examples given of the determination of quinol, aniline, phenylenediamine and *p*-aminodimethylaniline the chronopotentiometric technique. After u the electrode can be rapidly and reproducib cleaned by cathodic stripping. It cannot be us in soln. more alkaline than pH 5 nor in the prese of large concn. of anions which form very sta complexes with $Hg^+$, *e.g.*, oxalate, $SO_4^{2-}$, PO and $I^-$.

**II. Investigation of the characteristics of t mercury chloride film anode by voltage scan meth** T. Kuwana and R. N. Adams. *Ibid.*, 1959, **20** ( 60–67.—By using the voltage scan method, t mercury chloride film can be formed before t analysis is carried out. The electrode can then used in the presence of substances which form ve stable salts with $Hg^+$ or are strongly adsorbed the mercury surface. In addition a tenfold increa in sensitivity is achieved over the chronopotent metric method. For many organic molecules t film shows characteristics comparable to the pla num electrode and many of the $E_p$ (half-pe potential) values obtained are in good agreeme with the $E_{\frac{1}{2}}$ values for Pt under the same conditio of pH. W. T. CARTER

3852. **Use of a glass electrode for measuri sodium in biological systems.** S. M. Friedma J. D. Jamieson and C. L. Friedman (Dept. Ana Univ. Brit. Columbia, Vancouver, Canada). *Pr Soc. Exp. Biol. Med.*, 1958, **99** (3), 727–730.—T sodium electrode introduced by Eisermann, Ru and Casby (*Science*, 1957, **126**, 831) has been dev oped for biological use and is found particula useful for recording small changes in sodium con both in static and flowing systems.

B. P. BLOC

# ABBREVIATIONS

Certain abbreviations in everyday use are not included in the following list. When any doubt might arise from the use of an abbreviation or symbol the word is printed in full.

| | |
|---|---|
| alternating current | a.c. |
| ampere | amp. |
| Ångström unit | A |
| anhydrous | anhyd. |
| approximate, -ly | approx. |
| aqueous | aq. |
| atmospher-e, -ic. | atm. |
| boiling-point | b.p. |
| British thermal unit | B.Th.U. |
| calorie (large) | kg-cal. |
| calorie (small) | g-cal. |
| centimetre | cm |
| coefficient | coeff. |
| concentrated | conc. |
| concentration | concn. |
| constant | const. |
| corrected | (corr.) |
| crystalline | cryst. |
| crystallised | cryst. |
| cubic | cu. |
| current density | c.d |
| cycles per second | c/s |
| density | $\rho$ |
| density, relative | $d$ or wt. per ml |
| dilute | dil. |
| direct current | d.c. |
| distilled | dist. |
| ethylenediaminetetra-acetic acid | EDTA |
| electromotive force | e.m.f. |
| equivalent | equiv. |
| gram | g |
| gram-molecule | mole |
| half-wave potential | $E_{\frac{1}{2}}$ |
| hour | hr. |
| hydrogen ion exponent | pH |
| infra-red | i.r. |
| insoluble | insol. |
| international unit | i.u. |
| kilogram | kg |
| kilovolt | kV |
| kilowatt | kW |
| liquid | liq. |
| maxim-um, -a | max. |
| melting-point | m.p. |
| microgram | $\mu$g (not $\gamma$) |
| microlitre | $\mu$l |
| micromole | $\mu$mole |
| micron | $\mu$ |
| milliampere | mA |
| milli-equivalent | milli-equiv. |
| milligram | mg |
| millilitre | ml |
| millimetre | mm |
| millimicrogram | m$\mu$g |
| millimolar | m$M$ |
| millivolt | mV |
| minute (time) | min. |
| molar (concentration) | $M$ |
| molecul-e, -ar | mol. |
| normal (concentration) | $N$ |
| optical rotation | $\alpha_\lambda^t$ |
| ounce | oz |
| parts per million | p.p.m. |
| per cent. | % |
| per cent. (vol. in vol.) | % (v/v) |
| per cent. (wt. in vol.) | % (w/v) |
| per cent. (wt. in wt.) | % (w/w) |
| potential difference | p.d. |
| precipitate (as a noun) | ppt. |
| precipitated | pptd. |
| precipitating | pptg. |
| precipitation | pptn. |
| preparation | prep. |
| qualitative, -ly | qual. |
| quantitative, -ly | quant. |
| recrystallised | recryst. |
| refractive index | $n_\lambda^t$ |
| relative band speed | $R_F$ |
| relative humidity | r.h |
| revolutions per minute | r.p.m. |
| saponification value | sap. val. |
| saturated calomel electrode | S.C.E. |
| second (time) | sec. |
| soluble | sol. |
| solution | soln. |
| specific gravity | sp. gr. |
| specific rotation | $[\alpha]_\lambda^t$ |
| square centimetre | sq. cm |
| standard temp. and pressure | s.t.p. |
| temperature | temp. |
| ultra-violet | u.v. |
| vapour density | v.d. |
| vapour pressure | v.p. |
| volt | V |
| volume | vol. |
| watt | W |
| wavelength | $\lambda$ |
| weight | wt. |

In addition, the following symbols may be used in conjunction with numerical values or in mathematical expressions—

| | |
|---|---|
| greater than | $>$ |
| not greater than | $\ngtr$ |
| is proportional to | $\propto$ |
| less than | $<$ |
| not less than | $\nless$ |
| of the order of, approximately | $\simeq$ |

The principal Pharmacopoeias are denoted by B.P., U.S.P. or D.A.B., together with the identifying roman numeral or year.

Valency states are represented by a superscript roman numeral, *e.g.*, $Fe^{II}$, $Mo^{V}$. Substances in the ionic state are represented by $Na^+$, $Fe^{2+}$, $Fe^{3+}$, etc., for cations and by $Cl^-$, $SO_4^{2-}$ $PO_4^{3-}$, etc., for anions.

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